Ph.D. Thesis : B.V. Liengme

CORRECTIONS

page 8, line 14:

insert 'has an enthalpy of -153 kcal/mole'

page 11, penultimate line:

to read 'sintered nickel films'

page 16, equation 2:

to read $NH_3 \longrightarrow NH_2 + H$

page 16, equation 7:

to read $q(NH_3) =$

page 17, line 17:

to read 'this method'

page 17, line 22:

to read $E(NH_2 - M)$

page 28, last paragraph:

equation to read $NH_3 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \underset{Fe}{N} \overset{(5)}{\nearrow} N_2 \qquad \underset{(4)}{\overset{(3)}{\rightleftharpoons}} Fe_4N$

page 33, line 20:

to read $N(a) + \ldots H_2 \rightleftharpoons \ldots$

page 41, equation (1.5.1)

to read $N_2 + 3\ldots \longrightarrow 2NH_3$

page 44, line 11:

to read 'determined $\mathcal{D}_r$'

page 44, line 15:

to read $N_2^{30} + N_2^{28} \rightleftharpoons 2N_2^{29}$

page 48, line 2:

to read 'volta or contact potential different'

page 57:

fig.1.4 not 1.11

page 58, line 14:

to read 'discussed by Culver .....'

page 62, line 19:

to read '..... of -0.2 V at 77°K'

page 64, line 5:

to read '..... respectively. Which .....'

page 81, Table 3.1:

should read '77/90' not '90'

page 92, line 11:

to read 'and thus'

page 99, last line:

to read '..... of -0.5 V'

reference 179:

to read (1960)

THE MEASUREMENT OF SURFACE POTENTIALS AND THE STUDY OF HETEROGENEOUS CATALYSIS REACTIONS.

A Thesis

submitted for the Degree of Doctor of Philosophy

of the University of London

by

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November, 1964

ABSTRACT

The interaction of ammonia with evaporated W films has been investigated. The films were thrown in a vacuum of 10^{-8} torr at 90°K and annealed at 373°K. Surface potentials were measured using a space charge limited diode.

The surface potential of nitrogen on an evaporated W film was found to be -0.18 V at 90°K. It became increasingly negative with increasing temperature and reached a maximum of -0.5 V at 195°K. The surface potential of ammonia on W was found to be $+1.9 \pm 0.1$ V at 195°K and this decreased with increasing temperature. The interaction of hydrogen and nitrogen with ammonia has been investigated in order to examine the equilibrium :

$$NH_3 \rightleftharpoons NH_2 + H.$$

The evolution of hydrogen from a film saturated with ammonia has been examined. The kinetics of desorption could not be successfully treated by a second order equation for, although linear plots were obtained, these gave an unacceptably low value for the activation energy of desorption. The Elovich equation $dq/dt = a \exp(bq)$ was found to be applicable and gave an activation energy of ca 25 kcal.mole^{-1}.

The decomposition of hydrazine on evaporated tungsten films was also examined as a possible help in elucidating the mechanism of the decomposition of NH_3 on W. Ammonia and hydrogen were the products of decomposition. The ammonia was very rapidly desorbed

while hydrogen required an activation energy of ca 10 kcal $mole^{-1}$. Mechanism for ammonia and hydrazine decomposition are suggested.

ACKNOWLEDGMENTS

I thank Professor R.M. Barrer F.R.S. for the provision of laboratory facilities and the Department of Scientific and Industrial Research for a Research Studentship.

I am much indebted to Professor F.C. Tompkins F.R.S. and sincerely thank him for his kindness and guidance during many discussions.

To Mr. A. Madell, Mr. D. Alger and Mr. J. Preston and, indeed, all the technical staff of the Department I express my thanks. I also thank Mrs. Rycroft, Librarian, for her great help.

I am truly grateful to my mother-in-law, Mrs. U.O. Fowler, for typing this thesis and for many other kindnesses.

Finally I wish to thank all my colleagues in Room 124 for their friendship and help.

CONTENTS

CHAPTER I

INTRODUCTION

The Catalytic Synthesis and Decomposition of Ammonia

Frankenburg[1] has remarked that the catalytic synthesis of ammonia from its elements is a landmark in the development of catalytic processes. Here is an example of theory leading experiment. Early attempts to synthesise ammonia met with failure but, as the principles of equilibria became clear, more favourable conditions were used. These experiments finally resulted in 1908 in the Harber process. A review of the considerable amount of research undertaken since 1940 into the problem of understanding the process has been given by Bokhoven et al[2]. It is noteworthy that even in 1904 the superiority of iron over other catalysts was established; indeed, the reaction of nitrogen and hydrogen over iron has been studied perhaps more intensively than any other catalytic process[3]. Notwithstanding all this activity the detailed mechanism of the catalytic synthesis is as yet not satisfactorily understood.

Although the synthesis is stoichiometrically a simple one

$$N_2 + 3H_2 \rightarrow 2NH_3$$

the actual surface reaction takes place stepwise. The reaction of greatest interest is naturally that which limits the catalyst's output in the slowest or rate determining step. *A priori* this

might be the adsorption of nitrogen or hydrogen, the desorption of ammonia or one of the hydrogenation steps.

1.1. The Adsorption of Hydrogen

As the rate of chemisorption of hydrogen on iron catalyst was found to be rapid[1] even at temperatures well below that necessary for ammonia synthesis, this reaction was discounted as the rate determining step. More recently, however, hydrogen has been reported[3] to be chemisorbed in three differently bound states (see § 1.6.4). It is possible, but not demonstrated, that one of these may be chemisorbed slowly and that this state only may participate in the synthesis reaction. If this were so the rate of adsorption of only that species would have to be determined and compared with the rate of ammonia synthesis under catalytic conditions.

1.2. The Adsorption and Desorption of Ammonia

1.2.1. Early Decomposition Studies

In studying the decomposition of ammonia some investigators used electrically heated wires (4 to 9) while others (10 to 14) worked with metal powders. In the former case the products were hydrogen and nitrogen whereas powders yielded only hydrogen as the nitrogen formed was held chemisorbed on the solid. The poor state of vacuum technology at that time makes some of these results suspect. Powders were especially difficult to outgas.

Frankenburger[10] noted that the decomposition kinetics of ammonia over tungsten powder could be analysed as a mixture of first and second order reactions. On fresh powder the second order reaction predominated but as the surface became blocked "with nitride" the reaction rate decreased and became increasingly first order. Finally the surface was completely ineffective in decomposing ammonia. Deliberate poisoning by oxygen also produced first order kinetics. These experiments were conducted in the range 90° - 200°C.

Experiments (4 to 9) with heated wires generally involved high temperatures. Ammonia decomposition followed zero order kinetics in all reported cases. These authors have also evaluated activation energies (ΔE_d) for decomposition. Barrer[9] has pointed out that the accurate measurement of temperatures in these experiments was difficult and this explains the wide variation in reported values of ΔE_d as summarised in table 1.1. which includes decomposition experiments carried out, before 1946, on W and Mo.

Recent results for the decomposition of ammonia on other metals are discussed later. In table 1.3 (p.38) the activation energies for decomposition are given.

Table 1.1.

Decomposition Energies

Catalyst	Worker	ΔE_d (kcal/mole)	Temperature measurement
W wire	Hinshelwood (4)	38.7	Resistance
"	Taylor (5)	35.0	Resistance
"	Kunsman (6)	47.3	Optical pyrometer
"	Hailes (7)	26.3	Resistance
"	Perevesenseff (8)	42.1	Optical pyrometer
"	Barrer (9)	42.2	Compensating filaments
W powder	Frankenburger (10)	12.0	-
Mo wire	Burk (15)	53.2	-
"	Kunsman (6)	42.7 (31.8)	-
Mo powder	Kiperman (16)	42.5	-

Kunsman et al (6a) have recorded a variation of ΔE with temperature.

1.2.2. Adsorption studies

The investigation of desorption from a synthesis catalyst of ammonia per se is difficult for hydrogen and nitrogen will result because a catalyst must necessarily facilitate both the forward and backward reaction of an equilibrium reaction. Thus there is a paucity of data on ammonia adsorption and

desorption. Dew and Taylor[17] reported the initial heat of adsorption of ammonia on iron to be 16 kcal/mole. This suggests a rapid desorption of ammonia at high temperatures. They also observed a high antebatic dependence of the heat of adsorption upon the coverage.

Wahba and Kemball[19] have measured calorimetrically the heat of adsorption of ammonia on evaporated metal films of nickel, iron and tungsten at 21°C. The values of the initial heats were

Ni 37 ± 1 kcal/mole

Fe 45 ± 2 kcal/mole

W 72 ± 2 kcal/mole.

In all cases $d\Delta H/d\theta$ was high and with iron and tungsten at substantial ammonia coverages hydrogen was evolved. The rate adsorption of ammonia was lower than the rate of hydrogen adsorption especially for nickel.

As the dissociation energy $E(H_2N - H)$ is 104 kcal/mole[23] while $E(H - H)$ is 103 kcal/mole and, furthermore, as the differential heat curves for these two gases on a given nickel are similar it seems probable that metals which can dissociatively chemisorb hydrogen can adsorb ammonia as an amino radical and hydrogen atom provided the strength of the $M - NH_2$ bond is not substantially less than that of $M - H$.

The results for hydrogen and ammonia on nickel[19] seem to fit this hypothesis. The greater initial heat of adsorption of

ammonia may be the result of the bond strength Ni - NH_2 being greater than that of Ni - H. The slower rate of ammonia uptake could reflect a slightly higher activation energy of adsorption. However, this observation may be attributable to the slow diffusion of ammonia through the cold trap protecting the film. The greater decrease of heat with coverage, together with the smaller amount adsorbed, and the observation that a nickel film saturated with ammonia can still adsorb hydrogen could be accounted for in terms of either steric hindrance from the large amino radical or a large co-operative dipole interaction.

The adsorption of ammonia on nickel films[19] differed from that on iron and tungsten film in two aspects. Firstly, although the initial ΔH for ammonia on nickel was greater than the value of hydrogen, the two $\Delta H/\theta$ curves crossed at about $\theta = 0.5$. With iron and tungsten the ammonia curve was always above the hydrogen line. Secondly, adsorption of ammonia at 21°C on W & Fe resulted in an evolution of hydrogen at high coverages, nickel did not give hydrogen. However, Singleton et al[24] have shown that an ammonia pressure of 2 - 3 torr over a nickel film gave rise to a hydrogen pressure of 9×10^{-4} torr.

The evolution of hydrogen from ammonia, adsorbed as NH_2 and H, would require certain energy relationships[18]. Writing the adsorption processes as :-

$$NH_3 + 2M \rightarrow M - NH_2 + M - H + q_A \qquad (1.2.1)$$

$$H_2 + 2M \rightarrow 2M - H + q_H \qquad (1.2.2)$$

The formation of hydrogen is then suggested to take place as

$$NH_3 + NH_2 - M + H - M \rightarrow 2(NH_3 - M) + H_2 + q_D \qquad (1.2.3)$$

If these reactions take place under similar coverage conditions it follows that

$$q_D = q_A - q_H \qquad (1.2.4)$$

The entropy difference between an adsorbed hydrogen atom and an adsorbed amino radical will be very small and therefore, at equal pressures of H_2 and NH_3, reaction (1.2.3) will have an entropy change equal to the difference in the standard free energies of H_2 and NH_3 at 21°C, i.e. $\Delta S_D = -15$ cal/deg., hence $-T\Delta S_D = 4.4$ kcal/mole. It therefore follows that the evolution of hydrogen will be substantial if $q_D \gg 5$ kcal/mole, i.e. if the heat of adsorption of ammonia is at least 5 kcal/mole greater than that of hydrogen. A second condition for the reaction to take place is that the coverage must be high enough for the equilibrium pressure of hydrogen to be appreciable. These two conditions are met in the cases where hydrogen was evolved. However, the value of 5 kcal/mole was calculated for a system having equal pressures of ammonia and hydrogen and this does not seem to be the experimental condition.

Against the hypothesis of ammonia being chemisorbed as amino radicals and hydrogen atoms is the fact that if n is number of adsorbed ammonia molecules such a mechanism would give a maximum of ½ n hydrogen molecules whereas both iron and tungsten gave about

$^3/_4$ n hydrogen molecules. This suggests further dehydrogenation of the amino radical (NH_2) to an amino radical (NH) or even nitrogen atom. The observation[20] that the deuterium/ammonia exchange reaction takes place one hydrogen atom at a time indicates that the $-NH_2$ radical requires an activation energy for further decomposition. Further evidence for $-NH_2$ decomposition is that tungsten continued to evolve hydrogen when the ammonia pressure was small[19].

The existence of ammonium ions (NH_4^+) on the surface of a catalyst performing ammonia/deuterium exchange has been shown to be possible to a limited extent[20]. The reaction

$$NH_3 + H^+ \rightarrow NH_4^+$$

has an enthalpy of 209 kcal/mole[25] and therefore the reaction

$$NH_3 + \tfrac{1}{2}H_2 \rightarrow NH_4^+ + e.$$

The ionic radius is 1.45Å[26] and, if we assume mirror image charge attraction, the heat of adsorption would be 55 kcal/mole. The electron entering the metal will release energy equivalent to the work function of the metal. For catalytic metals this is always greater than 100 kcal/mole. Hence it is not impossible to form NH_4^+ ions from hydrogen and ammonia on a surface. But there is no formal evidence for the existence of such ions. Kinetic data for exchange are not sufficient to distinguish between a mechanism involving $-NH_2$ and one involving NH_4^+. Kemball[20] has suggested the correlation between the activation energy for D_2/NH_3 exchange and the work function of the catalyst

(see fig.1.1) to indicate the possibility that NH_4^+ might be involved.

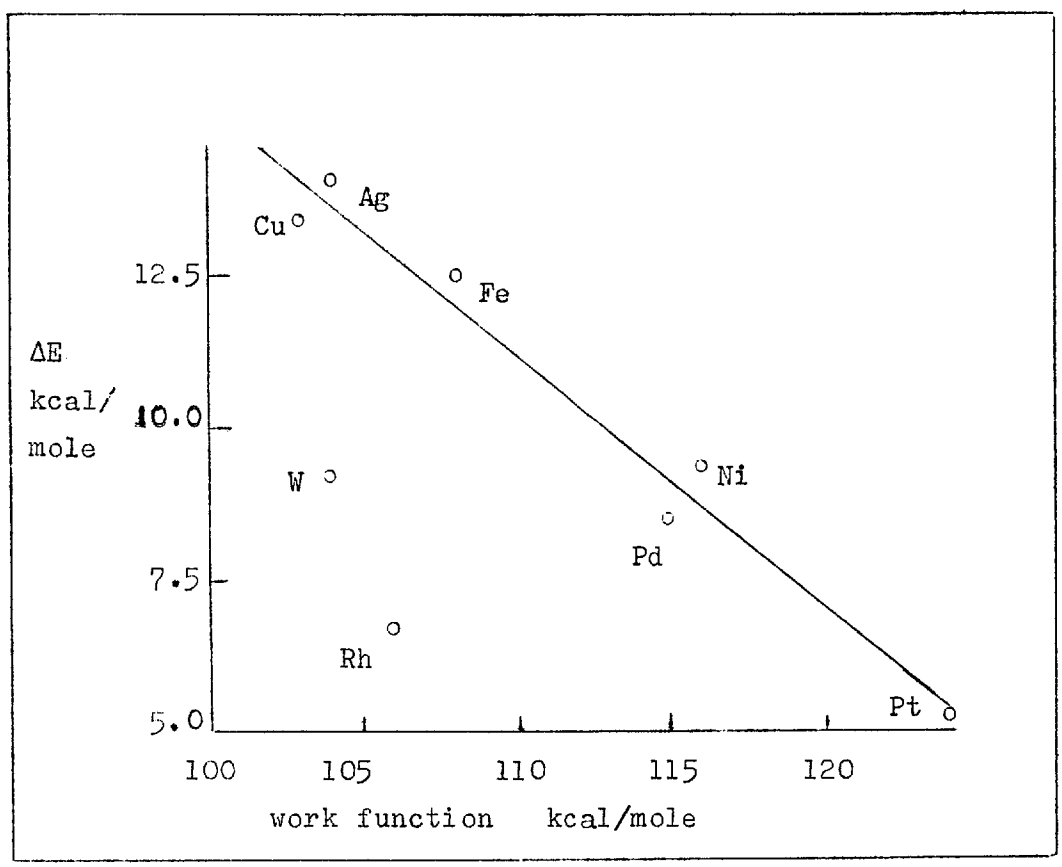

Fig.1.1

1.2.3. Exchange reactions with ammonia *

Exchange between deuterium and ammonia on promoted iron has been shown to occur[27,28] at a temperature well below that necessary for ammonia decomposition. This has been taken to indicate that neither the rate of hydrogen adsorption nor the rate of ammonia decomposition is the rate controlling step in ammonia synthesis.

Following a previous experiment using nickel films[18] Komball has made an extensive study of this exchange on eight evaporated metal films (Pt, Rh, Pd, Ni, W, Fe, Ag and Cu). The most striking feature of his results was that the relative amounts of the deutero ammonias, measured by a mass spectrometer, were independent of the catalyst used. Only one parameter - the initial rate of production of NP_2D was needed to define completely the various amounts and, by using an arbitrary time scale he was able to plot (fig.1.2) the production of each deutero ammonia from the various catalysts on one curve. Making the following assumptions

(i) one hydrogen atom of the ammonia molecule was exchanged at a time,

(ii) the a priori change of hydrogen exchange was equal for protium and deuterium,

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* In this section the "hydrogen" or H denotes the element generally. The isotopes are differentiated as P, protium and D, deuterium.

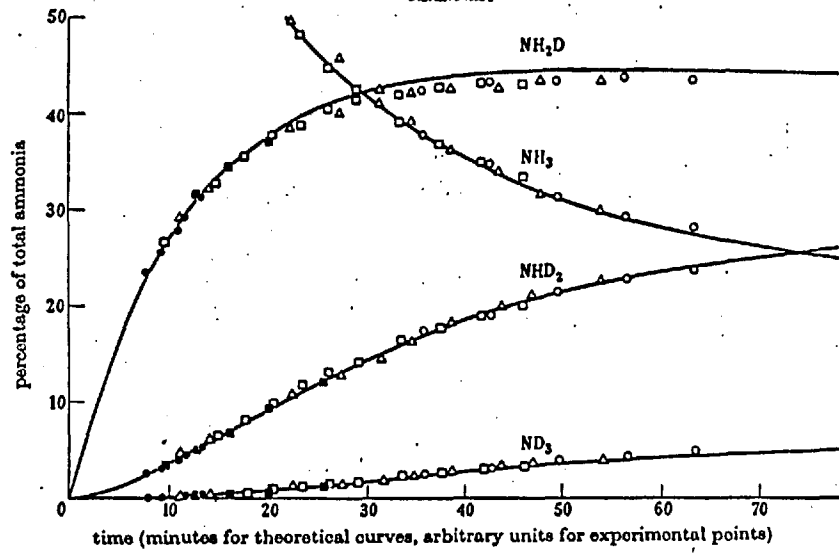


FIG.1.2 The relative amounts of the deutero-ammonias formed from equimolar mixtures of ammonia and deuterium. ——, theoretical amounts obtained by integrating equations (8); △, 8·9 mg nickel at 115·3° C, 1 unit = 0·485 min; ○, 3·2 mg platinum at −24·1° C, 1 unit = 0·290 min; □, 6·9 mg tungsten at 143·0° C, 1 unit = 0·700 min; ●, 2·9 mg silver at 208° C, 1 unit = 2·90 min; ■, 6·6 mg copper at 245° C, 1 unit = 1·89 min.

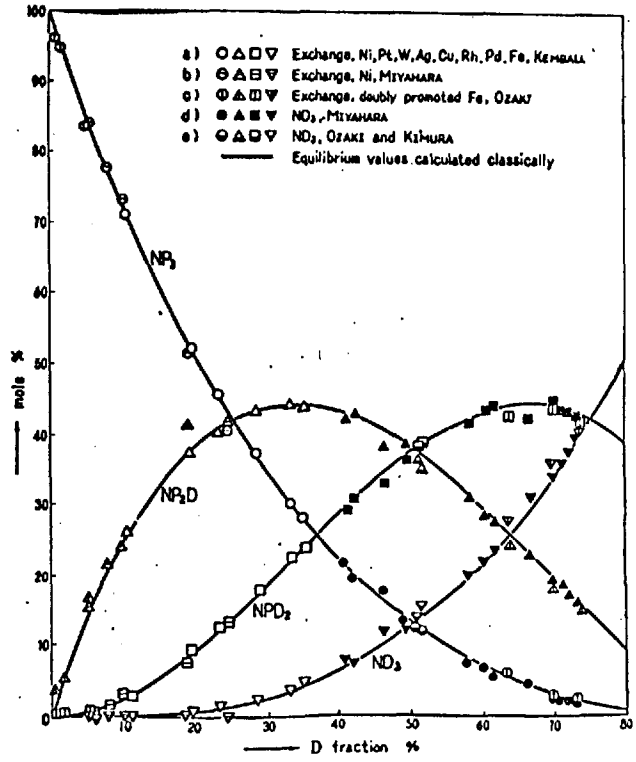


FIG. 1.3 The results of mass spectrometric measurements of ND_3 in comparison with those of the resultant ammonia of catalysed exchange reaction between NH_3 and D_2 in the presence of metallic catalysts.

(iii) there is no isotope effect in the velocity constants differentiating the deutero ammonias,

he was able to set up and solve four differential equations representing the production of NP_3, NP_2D, NPD_2 and ND_3. It will be seen from fig.1.2 that the experimental points fit the theoretical lines very well.

The values of the activation energies for exchange obtained by Kemball[20] using unsintered films differ considerably from those of Singleton et al[24] who worked with unsintered films. These are summarised in table 1.2.

Table 1.2

Activation Energies for Exchange NP_3/D_2

Metal	Kemball[20]	Singleton et al[24]
Pt	5.2 kcal/mole	
Rh	6.7 "	
Pd	8.5 "	
Ni	9.3 "	15 kcal/mole
W	9.2 "	15 "
Fe	12.5 "	21 "
Cu	13.4 "	
Ag	14.1 "	

But Kemball[20] has also performed one experiment with a sintered film and he did not find a great change in ΔE. He also considers the ideal straight line obtained in the plot of log k against $1/T^{\circ}K$

shows sintering is not of great importance. Furthermore, there is evidence[29] that tungsten films are sintered when thrown because of the heat emitted by the evaporating filament and that further heat treatment has no effect upon the surface area at least up to 500°C.

Kemball has discussed the possible mechanisms for the rate determining step of the exchange. He considers it may be a suitable combination of two or more of the half-mechanisms :

A) $NP_3 \downarrow M + D\ M \rightarrow$

B) $NP_3 \vdots M + D\ M \rightarrow$

C) $NP_3D^+ \vdots M + M \rightarrow$

D) $D_2 \vdots M + NP_2\ M \rightarrow$

Weber and Laider[30] who worked with an iron catalyst thought A to be the mechanism. Step B is the reaction between a gaseous or physically adsorbed ammonia molecule and a chemisorbed deuterium atom. C represents the decomposition of an ammonium ion, and D the reaction between a gaseous or physically adsorbed deuterium molecule and a chemisorbed amino radical. The possible combinations are AA, BB, AB, AC, AD, BC and BD. Other combinations are excluded, CC because it does not give exchange; CD and DD as they involve exchange of more than one hydrogen atom at a time.

It was not possible to state which mechanism is most plausible because if the adsorption of the various species is given by Langmuir equations the four reactions A, B, C and D will all depend on the same kinetic expressions. However, Kemball[20] does consider the correlation between activation energy and work function (fig.1.1) as proof that NH_4^+ ions might exist on the surface.

Recently the whole basis of Kemball's[20] analysis has been questioned[31]. Infra-red spectrometry studies[32] showed that an equimolar mixture of NP_3 and ND_3 in a glass vessel at room temperature, was converted into an equilibrium mixture of deutero-ammonias within a week of mixing. In a re-examination[33] of this reaction in a vessel outgassed at 300°C and 1 x 10^6 torr, the I.R. spectrum taken just after mixing showed hydrogen exchange had taken place and the spectrum taken after heating the sample at 200°C for 5 minutes was identical to the first. This indicated that randomization of hydrogen in ammonia was instantaneous. Two independent laboratories[31] have reported that ND_3 placed in a mass spectrometer was very rapidly converted into the equilibrium mixture identical to that obtained by exchange between deuterium and ammonia on a catalyst as studied by Kemball[20]. Figure 1.3 shows that the experimental data obtained by the various workers are identical. This has led Miyahara et al[31] to conclude that Kemball's measurements are not relevant to the catalysts and consequently no reaction mechanism, such as unistep replacement, can be validly deduced from them. However, if the spectrometer

caused the randomization one is not able to explain why Kemball obtained different data with differing films for the mass spectrometer was the same throughout.

It still remained to explain why ND_3 was randomized in the mass spectrometer. The observation[33] that there was no significant exchange between D_2 and NP_3 in the glass vessel or mass spectrometer at 150°C was used[29] as evidence that any protium chemisorbed on the glass vessel could not have been the cause. Also, as the different mass spectrometer used by the various investigators were all operated at low electron accelerating voltages giving spectural peaks only for NH_3^+, fragmentation and subsequently recombination could not be the cause of the effect. Miyahara et al[29] were thus forced to conjecture that water chemisorbed on the glass and/or metal parts of the spectrometer was the source of protium in their experiments. While it seems presumptuous to assume that Kemball's apparatus was similarly contaminated, it must be pointed out that in a report of other work Kemball[21] does mention that "the mass 17 peak heights were corrected for the amount of OH^+ ion formed by fragmentation of water present as a 'background' in the spectrometer". The point could be argued categorically only if a "blank run" were carried out in the catalytic experiments.

In re-assessing his earlier results[33] Miyahara[35] states that, although the mass spectrometer caused rapid hydrogen randomization in ammonia and thus removed any meaning from the

relative abundances of the deutero-ammonias, the relative abundances of P_2, D_2 and PD were practically unaffected. He has used their distribution to analyse the mechanism of exchange and has calculated the exchange activation energy over nickel as 8.9 kcal/mole. This value is in good agreement with Kemball's[20] value of 9.2 kcal/mole. Miyahara stresses this agreement as Kemball's value is calculated from the initial stage of the D_2/NP_3 exchange when the deutero-ammonia formed was practically all NP_2D. Presumably Miyahara was claiming that the "rapid" randomization caused by the mass-spectrometer is not rapid enough to over-ride the catalytic effect of the metal film at this stage of the reaction.

Singleton et al[24] in their exchange experiments did not measure the deutero-ammonias but the D_2/P_2 ratio hence the conclusions are unaffected by the new observation[31].

Another interesting point is raised by Kemball's[20] exchange experiments. This work was conducted with evaporated metal films of Pt, Rh, Ni, W, Fe, Ag and Cu (and also oxidised W, Ni and Cu). The only experimental condition differentiating these metals is that the exchange was studied at $0^{\circ}C$ for all metal except copper and this was maintained at $-78^{\circ}C$ to prevent the film sintering. Neither copper or silver was singled out for any special remarks, indeed in a plot of activation energy against work function (fig.1.1) copper and silver follow the general pattern (and W and Rh lie far from the line). However, copper and silver differ from the other metals in being unable to chemisorb molecular

hydrogen. Indeed, hydrogen atoms adsorbed by copper at low temperature are desorbed as molecules at room temperature[162]. Thus Kemball's[19] hypothesis, that metals which adsorb hydrogen as atoms can adsorb ammonia as amino radicals and hydrogen atoms provide the M - NH_2 bond is not substantially less than the M - H bond, is not applicable in these cases.

Listing the following reaction with their enthalpy changes ΔH,

$$H_2 \longrightarrow H + H \qquad \Delta H = E(H - H) \qquad 1$$

$$NH_2 \longrightarrow NH_2 + H \qquad \Delta H = E(HN_2 - H) \qquad 2$$

$$H + M \longrightarrow M -- H \qquad \Delta H = E(M - H) \qquad 3$$

$$NH_2 + M \longrightarrow M - NH_2 \qquad \Delta H = E(M - NH_2) \qquad 4$$

The heat of dissociation adsorption of hydrogen at zero coverage will be given by

$$q_{H_2} = 2E(M - H) - E(H - H) \qquad 5$$

and similarly for ammonia

$$q_{NH_3} = E(M - H) + E(M - NH_2) - E(H_2N - H) \qquad 6$$

Since $E(H_2N - H) = 103$ and $E(H - H) = 104$ kcal/mole we may equate them and put :-

$$q_{NH_2} = E(M - H) + E(M - NH_2) - E(H - H) \qquad 7$$

whence

$$q_{NH_3} = 2x + q_{H_2} \qquad 8$$

where x is the difference $\{E(H_2N - H) - E(H - H)\}$. In the case of copper $q_{H_2} = 8$ kcal/mole (180) thus if q_{NH_3} is to have a reasonable value x must be large, i.e. the bond energy of M - NH_2 must be much greater than M - H. It is difficult to see why Cu - NH_2 and

Ag - NH_2 should be greater than the metal-amino radical bond for other metals. But it is puzzling that if Cu and Ag are differently adsorbed their kinetics fit the general treatment of Kemball. For the bond energy E(M - R) between metal M and atom or radical R Pauling[181] has given the formula :

$$E(M - R) = \tfrac{1}{2}\{E(M - M) + E(R - R)\} + 23.06\,(X_M - X_R)^2 \qquad (9)$$

The second term on the right allows for the ionic contribution to the bond energy as X_M and X_R are the respective electronegativities. The value of E(M - M) may be taken[182] as one-sixth the latent heat of vaporization of the metal. Eley[183] has suggested as an approximation that

$$X_M - X_R = \mu$$

when μ is the dipole moment of the bond M - R at $\theta \longrightarrow 0$. A better and experimentally easier approach was suggested by Stevenson[184] who put $X_M = 0.355\ \phi_M$ (ϕ_M is the work function of the metal, see §1.6.1) and used Pauling's electronegativity for X_R.

It is interesting to apply the method which gives heats of adsorption of hydrogen on various metals in excellent agreement with experimental values, to Kemball's[20] heats of ammonia adsorption. From eqn (5) we can readily calculate E(M - H). Using these values, Kemball's[20] q_{NH_3} values and Szwarc's[25] value of 104 kcal/moles for $E(H_2N\text{-}H)$, we may calculate from eqn (6) values for $E(H_2N - 4)$. If we now apply Pauling's equation (9) to the M - NH_2 bond it should be possible to calculate X_{NH_2}. To perform this calculation we have used one sixth of the latent heat of vaporization[185] to

obtain E(M - M). Work functions are taken from Culver and Tompkins[114]. For $E(H_2N - NH_2)$ the value of 60 kcal/mole was used. The various parameters used and X_{NH_2} so obtained are listed in table 1.

Table 1

Parameters		W	Fe	Ni
E(M - H)	kcal/g atom	74	67.5	66.5
q_{NH_3}	kcal/mole	75	45	37
$E(M - NH_2)$	kcal/g atom	101	81	74
λ	kcal/mole	191	83.9	88.9
ϕ	eV	4.5	4.77	5.03
χ_{NH_2}	as calculated	0.13	0.40	0.62

The wide variation in χ_{NH_2} is most unacceptable. While it might be suggested that this indicates that the model upon which it is based (i.e. dissociative adsorption) is incorrect the equation for $E(M - NH_2)$ is at the best a crude approximation in spite of the good agreement between $q_{(cal.)}$ and $q_{(expt.)}$ for $M - H_2$ systems.

1.3. The Adsorption of Nitrogen

1.3.1. Chemisorption of nitrogen

So far we have seen that the rate controlling step is unlikely to be the adsorption of hydrogen or the desorption of ammonia. The claim that nitrogen adsorption is the rate determining step is far more extensively documented. One fact which is taken as evidence[36] for this is that while many metals can catalyse hydrogenation only those capable of chemisorbing nitrogen atomically have a potential use as ammonia synthesis catalysts.

Nitrogen is chemisorbed by metal surfaces in a number of ways. Some metals, Fe[37], Co[38] and Ni[39] cannot dissociately chemisorb nitrogen but are capable at 78°K of weak, reversible adsorption. Pumping at room temperature will remove the nitrogen. With Ni the weak chemisorption is inhibited by a low coverage of atomic nitrogen (N atoms formed in the gas by a hot wire etc are adsorbed by a Ni surface). Selwood[40] has observed some loss of magnetization of nickel supported on silica at -78°C which cannot be interpreted as molecular adsorption. On iron filaments. at low temperatures the monolayer volume of nitrogen approximates to that of hydrogen[41] which suggests weakly chemisorbed nitrogen may be held as

$$\begin{matrix} N = N \\ | \quad | \\ M \quad M \end{matrix}$$

Only nitrogen held atomically can participate in ammonia synthesis and those metals of Group VIA, VIIA and VIII which have

sufficient d-orbitals, are capable of this. Generally there is an activation energy for adsorption of atomic nitrogen[36]. From the general theory of catalytic activity it is readily understandable that maximum activity is found with metals which chemisorb nitrogen most weakly[1]. The ability to chemisorb nitrogen in this way ceases after Group VIII. The tendency to effect formation of nitrogen atoms increases on passing from right to left across the transition series and this is shown by (1) an increase in the heats of chemisorption, (2) an increase in the tendency to bulk nitride and (3) the disappearance of the activation energy for chemisorption. All of which leaves Fe, Ru and Os as these metals having greatest activity in ammonia synthesis. Dissolved nitrogen atoms play no part in ammonia synthesis[2,24] but metallic nitrides are capable of ammonia synthesis and decomposition[42].

1.3.2. The States of Binding of Nitrogen on Tungsten

As long ago as 1931 Frankenburger[10] reported the existence of two forms of nitrogen adsorbed on tungsten. Ehrlich et al[43-47] have conducted an extensive study of the nature of the nitrogen species present on a tungsten surface. Using the flash desorption technique development by Becker and Hartman[48] it has been possible to measure the concentration and binding energies of the various species. Field emission microscopy studies have yielded surface potential and mobility information.

It has been shown that there are three species of nitrogen on tungsten. Two of these, α and β, are held by forces great enough to permit the term "chemisorbed" to describe them. The third state, γ, is held by dispersion forces, i.e. the γ state is physically adsorbed. We shall consider the properties of the three states.

β State

This is the primary adsorption species and at temperatures above 100°K most of the nitrogen exists in this state. In this state nitrogen is held as immobile atoms with a bond energy of circa 150 kcals/g atom.

Studies of the kinetics of adsorption of β nitrogen have shown that molecular nitrogen approaches the clean surface, it is initially held by dispersion forces before the homonuclear molecule dissociates into atoms. The sticking probability for formation of β nitrogen is a function of surface concentration $n\beta$ and temperature. The initial sticking probability for β nitrogen at 115°K is greater than at 300°K (0.38 and 0.29 respectively). The higher rate of adsorption at the lower temperature is due to binding of nitrogen in the γ state which is thus the precursor of the β state. At room temperature the γ state is not significantly populated and the rate of formation of β state is decreased.

The rate of formation of the β state is rapid at special active sites, perhaps lattice steps, and adsorption on these occurs

at temperatures as low as 80°K. Adsorption in the β state also occurs at other sites but the process has a higher activation energy which precludes chemisorption at 80°K. For example, at 115°K the initial adsorption of the state shows no sign of being an activated process but at higher surface concentration ($n\beta > 2 \times 10^{14}$ molecules cm^{-2}) the sticking probability falls below the higher temperature value indicating a low temperature activation barrier. This must be due to a different formation mechanism connected with the additional γ state. At 265°K saturation occurs at 2.8×10^{14} molecules cm^{-2} while at 115°K the maximum concentration falls to 2.25×10^{14} molecules cm^{-2}.

Complete desorption of the β state occurs at temperatures above 2000°K.

The α State

The structure of the gas burst evolved from the tungsten filament on heating shows the presence of a state held less energetically than the β state. This is the α state and is thought to be molecular and in this state the adsorption is irreversible and the population is independent of temperature or pressure.

The amount of nitrogen adsorbed in the α state is, for low coverage at least, a function of the amount in the β state. The constant relationship between n_α and n_β can be explained if the rate of formation of the α and β states have the same limiting step; such as diffusion to active sites and if the number of

α and β sites differ. Again, it could be explained if the number of α sites were a function of the populated β sites; i.e. if adsorption in the β state generated α sites. Differentiation between these hypotheses is possible by kinetic studies. The population n_α reaches a maximum value at a value of n_β which is somewhat larger than the value at which S_β becomes markedly dependent on n_β. When this dependence sets in there is a mechanistic change from a diffusion to a reaction controlled rate. The continuance of a linear relationship between n_α and n_β after such a change eliminates the possibility of a common controlling step.

The generation of α sites by occupancy of β sites would not be so eliminated. Roberts[50] has shown that adsorption of diatomic molecules without lateral interaction, in an immobile layer gives rise to a number of single, unoccupied sites. Spacially, such sites could not accommodate both atoms of a molecule, but energetically could hold, albeit weakly, the molecule. Ehrlich suggested that the β nitrogen does not greatly differ from this model because the atoms formed by the rupture of the N≡N bond are immobile and therefore held on adjacent sites. The single unoccupied sites so formed could be the α sites. Furthermore, the strongly bound β state would induce surface states[51] which could hold a nitrogen molecule by one electron bond as envisaged by Pollard[52]. However, this would mean that n_α would increase rapidly with n_β whereas a linear relationship is obtained experimentally. This difficulty may be avoided by

restricting the β nitrogen to lattice steps; in this way the number of nearest neighbours is decreased and so would the n_α dependence on n_β.

Although the exact nature of the α state is still unknown we can state that the α state is thermodynamically less stable than the β state. As conversion $\alpha \rightarrow \beta$ does not occur there must be a barrier. to prevent this. Physically this could mean that the α sites are surrounded by sites on which β cannot be formed. Then the barrier to surface migration must be the same magnitude as the activation energy for evaporation.

Complete denudation of the α state occurs at temperatures in excess of 400°K.

The γ State

At temperatures below 110°K the third state becomes sensibly populated. At a temperature of 80°K the γ state is the most densely populated state and competes successfully with chemisorption.

The bond energy of this state is 9 kcal/mole and nitrogen retains its molecular identity. Although the polarizability of nitrogen is half that of xenon the bond energies are comparable. Thus the force of adhesion must be other than van der Waals'.

As in the case of the α state the population of the γ sites is dependent upon n_β. However, whereas n_α increased linearly with n_β, n_γ increases more rapidly and the saturation population in greater than n_α by a factor of 30. At temperatures above 80°K it may be that the γ state exists as the precursor to the β state.

Very significant changes in n_γ can be achieved by adsorption of nitrogen at room temperature prior to adsorption at 115°K. During the adsorption at $T \sim 115^\circ K$ the initial percentage of γ nitrogen is low but at higher coverage it becomes predominant and towards the end assumes overwhelming proportions. At a given concentration of β, the number of γ molecules is fixed and independent of pressure.

1.3.3. Nitrogen adsorption as the rate determining step

Adsorption rate measurements

The rate of chemisorption of nitrogen was first suggested to be the rate determining step in ammonia synthesis by Emmett and Brunauer[53,54] following measurements made on technical iron catalysts. A comparison[55] of the rate of chemisorption of nitrogen with the rate of ammonia synthesis on Fe - Mo catalysts was further evidence for this. The simultaneous measurements of these parameters is difficult because the rate of nitrogen uptake is highly dependent on the surface nitrogen coverage[56], the value of which, during a synthesis reaction, is generally unknown. This difficulty was surmounted[57] by first making a gravimetric determination of the dependence of uptake on coverage and then, in an ammonia synthesis, making simultaneous estimation of (i) the rate of nitrogen adsorption, (ii) coverage (gravimetrically) and (iii) the rate of ammonia production. Except at low temperatures there was good correlation between the two rates.

Exchange Experiments

The isotopic exchange reaction

$$N^{14}N^{14} + N^{15}N^{15} \rightleftharpoons 2N^{14}N^{15}$$

has been the subject of numerous studies. The first of these[58] produced a paradox. Whereas a doubly promoted iron catalyst was capable of ammonia synthesis and decomposition at 400°C it did not produce exchange at a measurable rate until the temperature was 460°C But hydrogen improved the efficiency as an exchange catalyst. When the experiment was repeated[60] exchange was observed but it was still some ten times slower than expected from calculations based on desorption rates[61]. On a singly promoted catalyst however the exchange rate was in good agreement with these calculations. Again the enhancing effect of hydrogen was detected and a corresponding poisoning effect of oxygen observed. The failure of Jovis and Taylor's[58] catalyst was thus attributed to incomplete reduction of the catalyst. This was confirmed in experiments[59] which showed that a promoted catalyst, found to be almost in active to exchange, became much more active after prolonged reduction. Even so those catalysts inactive to exchange were able to synthesise ammonia. The observation that more rapid exchange occurred with singly than with doubly promoted iron may be coupled with the observation[62] that unpromoted iron gave more rapid exchange than promoted iron. This is perplexing as promotion, by definition, enhances the ammonia synthesis activity. However, Boreskov et al[63] found that the specific activity for

exchange on promoted catalysts was much greater than that on unpromoted catalysts and that the absolute velocity of ammonia synthesis under the same conditions was in good agreement with the exchange velocity over singly promoted and pure iron catalysts. But doubly promoted catalysts again gave an exchange rate less than the synthesis rate. Gorbunov and Boreskov[64] attribute this effect to the well known difficulty of obtaining complete reduction with doubly promoted catalysts.

In spite of this explanation of low exchange rates, doubly promoted catalysts are still very active in ammonia synthesis. It seems most improbable that there is one rate determining step for singly promoted catalysts and another for those doubly promoted. King[65] has advanced a hypothesis that there might be different nitrogen specie on these catalysts. Obviously exchange will occur only if the nitrogen is atomically held. It might be that a molecular N_2 state on doubly promoted iron and that its adsorption is rate determining. A further suggestion is that the slow exchange rate might merely reflect a low mobility of the nitrogen atoms on the surface.

Decomposition Experiments

Further evidence for the rate of chemisorption being the rate determining step is provided by catalytic decomposition experiments over evaporated metal films at temperatures between 250°C and 740°C using a mass spectrometer[21]. Kinetic results on iron showed that the rate of ammonia decomposition was controlled by the rate

of nitrogen desorption from the catalyst surface. The close similarity of the activation energies for decomposition (38.8 kcal/moles) and for the decomposition of the nitride phase in the catalyst to gaseous nitrogen (38.6 kcal/moles) was taken to point to a common rate determining step. The decomposition of iron nitride requires two steps, the migration of nitrogen atoms through the iron lattice and desorption of nitrogen gas. The activation energy of 38.6 kcal/mole is associated with desorption because hydrogenation of iron nitride to ammonia also includes the migration and required an activation energy of about 14 kcal/mole. This also indicated that the addition of H atoms to N atoms or NH and NH_2 radicals is rapid and none of these hydrogenations could be rate determining. Since the formation of FeN_4 proceeds at a rate which is more rapid than the production of nitrogen the removal of the atoms from adsorbed NH_3 to produce adsorbed N atoms is a relatively rapid process and faster than the rate of formation of N_2. Summarised diagrammatically :

$$NH_3 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \underset{Fe}{\overset{N_2\ (5)}{\|}} \underset{(4)}{\overset{(3)}{\rightleftharpoons}} Fe_4N$$

Steps (1) and (4) are rapid compared to (5). The decomposition of ϵ nitride (Fe_3N to Fe_2N) has been shown[66] to be about 10^4 times slower than the hydrogenation. The decomposition had an activation energy of 42.1 kcal/mole.

1.4. The Temkin and Pyzhev Isotherm

1.4.1. The Derivation

The concepts introduced in 1939 by Temkin and Pyzhev[67] concerning the kinetics of ammonia synthesis have subsequently dominated the study of these reactions. These authors set out to derive a rate expression which was both mechanistically justifiable and capable of expression the known experimental dependence of the rate of synthesis on the partial pressure of the three reacting gases.

Their hypothesis was based on three assumptions, namely that

(a) the rate of chemisorption of nitrogen is the rate determining step. Although they assumed dissociative adsorption the state of the nitrogen species does not affect the conclusions,

(b) the presence of hydrogen and ammonia does not alter the nitrogen adsorption. This assumption will be discussed later.

(c) as a result of surface heterogeneity of activation energies of nitrogen adsorption and desorption (and hence the heat of adsorption) have a linear antebatic dependence on the coverage :

$$\Delta H_a = \Delta H_o \ (1 - \gamma\theta) \qquad 1.4.1.$$

hence the rates of adsorption (r_a) and desorption (r_d) are given by

$$r_a = k_a P_N \exp(-g\theta_N) \qquad 1.4.2.$$

$$r_d = k_d \exp(h\theta_N) \qquad 1.4.3.$$

where P_N = nitrogen pressure, θ_N the nitrogen atom coverage and k_a, k_d, g and h are constants. At equilibrium ($r_a = r_d$) equation 1.4.2 and 1.4.3 give the isotherm :-

$$\theta = {}^{1}/_{f} \ln aP_N \qquad 1.4.3.$$

where $f = g + h$ and $a = {}^{k_a}/_{k_d}$. If assumption (b) holds true then the rate of formation of ammonia (r_s) will be given by :-

$$r_s = r_a - r_d$$
$$= k_a P_N \exp(-g\theta_N) - k_d \exp(h\theta_N) \qquad 1.4.4.$$

A hypothetical pressure P_N^x is defined :

$$P_N^* = K_e \frac{P_A^2}{P_H^3} \qquad 1.4.5.$$

where P_A and P_H are the partial pressures of ammonia and hydrogen respectively and K_e the equilibrium constant for the reaction :

$$2NH_3 \rightleftharpoons N_2 + 3H_2 \qquad 1.4.6.$$

Thus P_N^* may be thought of as the pressure of nitrogen that would be present if equilibrium was obtained between ammonia, hydrogen and nitrogen in the gas phase.

The overall hydrogenation of nitrogen on the surface

$$2N(a) + 3H_2 \rightleftharpoons 2NH_3 \qquad 1.4.7.$$

is considered to be in equilibrium hence there will be an equilibrium between the adsorbed and gas phase hydrogen and the adsorbed and gas phase ammonia. Temkin and Pyzhev[67] thus consider P_N^* to be the equilibrium pressure of the adsorbed nitrogen.

The Temkin-Pyzher treatment further enables the activation energy E for ammonia decomposition to be estimated since

$$E = E_a + \alpha(-\Delta H_a) + (1 - \alpha)(-\Delta H)$$

where E_a and $-\Delta H_a$ are respectively the activation energy and the heat of adsorption of nitrogen at zero coverage, and $-\Delta H$ is the enthalpy change accompanying the synthesis.

Numerous investigators[2] have reported that their data can be fitted to the Temkin equation, at least over a range of conditions. Temkin and Kipermann have reported that with Mo[16], W[69] and Ru[70] between 500 and 700°C the kinetic of synthesis conform to Temkin-Puzhey kinetics, but with Os[71] the agreement was poor. In the case of iron, the most extensively studied catalyst, agreement or not depends greatly upon the conditions of the synthesis[36].

One aspect which is not entirely satisfactory is the lack of constancy of α. That the derivation is not applicable over the complete coverage range was explained by Brunauer et al[61]. They pointed out that the isotherm 1.4.3. does not have limits of $\theta_N = 0$ at $P_N = 0$ and $\theta_N = 1$ as $P \longrightarrow \infty$. To extend the usefulness of the theory they suggested putting

$$r_a = k_a \exp P_N \exp (g\theta_N) - \exp (g) \qquad 1.4.10.$$

$$r_d = k_d \exp h\theta_N - 1 \qquad 1.4.11.$$

which would give

$$\theta_N = \frac{1}{f} \ln \frac{1 + aP_N}{1 + aP_N \exp (-f)} \qquad 1.4.12.$$

This isotherm successfully describes nitrogen adsorption on doubly promoted iron catalysts[61]. At sufficiently low value of θ (1.4.12) reduces to (1.4.2). Neglecting the back reaction the rate of synthesis is given

$$\overrightarrow{r} = k_a P_N \exp (- g\theta) \qquad 1.4.13.$$

The adsorption isotherm may then be obtained using 1.4.12 as

$$\theta = \frac{1}{f} \ln \left[\frac{1 + a K_\theta P_A^2 / P_H^3}{1 + e^{-f} a K_\theta P_N^2 / P_H^3} \right]$$

As it has been shown[51] that $f \simeq 20, e^{-f}$ must be very small and it is justifiable to assume

$$e^{-f}\ aK_e\ P_A^2/P_H^3 \ll 1.$$

From equation 1.4.13

$$\vec{r} = \frac{k\ P_N}{(1 + aK\ P_A^2/P_H^3)^{\alpha}} \qquad 1.4.14.$$

At high coverage and hence high efficiencies we may assume

$$aK\ P_A^2/P_H^3 \gg 1$$

and (1.4.14) reduces to the original equation of Temkin and Pyzher.

1.4.2. The Validity of the Temkin-Pyzhey Theory

The validity of Temkin and Pyzhey's original assumptions and the subsequent derivation would be vindicated if the rate constant k_a' were found to be (a) independent of the space velocity and (b) unchanged if hydrogen were replaced by deuterium. Furthermore the activation energy and the value of the constant α should be similarly invariant.

Ozacki et al[72] have examined condition (b) in experiments using D_2 in place of H_2, at constant total pressure P and, by using a low temperature and hence a low conversion rate, maintaining the stoichiometric condition $P_H/P_N = 3$. Under these conditions the back reaction may be neglected and the rate of synthesis (1.4.9) may be re-written :

$$\frac{dy}{dt} = \frac{C_1 P^{(3\alpha+1)}}{y^{2\alpha}} \qquad 1.4.15.$$

where y is the ammonia pressure $C_1 = (1/4)\ (3/4)^{\alpha}$. As the contact time, t, is proportional to the ratio of total pressure/flow rate, i.e. (P/V)

$$\frac{dy}{dt} = \frac{C}{y^{2\alpha}}$$

where $C = C_1 P^{(3\alpha+2)}$

Integration of this gives

$$y^{2\alpha+1} = \frac{(2\alpha+1)\ C}{v}$$

A plot of ln y against ln $(1/v)$ should give a straight line of slope $(2\alpha + 1)$. Ozacki found that

(i) α decreased with decreasing efficiency i.e. decreasing temperature,

(ii) C varied almost linearly with P whereas theory predicted that $C \approx P^{(3\alpha + 2)}$.

However, it has been shown[72] that the concept of surface heterogeneity used by Temkin and Pyzhev is not essential. On a homogeneous surface the rate of dissociative adsorption of nitrogen, equal to the rate of nitrogen, is given by

$$r = k' P_N (1 - \theta_N)^2$$

If K is the equilibrium constant for the reaction

$$N_a + 1.5\ N_2 \rightleftharpoons NH_3$$

then the Langmuir isotherm gives

$$\theta_N = \frac{K\ P_A/P_H^{1.5}}{1 + K\ P_A/P_H^{1.5}}$$

the rate expression then becomes

$$r = \frac{k' P_N}{\left[1 + K P_A / P_H^{1.5}\right]^2}$$

which is closely related to the equation of Temkin and Pyzhev. Written in the form

$$\frac{dy_A}{d(1/v)} = \frac{k}{(1 + a y_A)^2} ,$$

where k is proportional the rate constant k' for the adsorption of nitrogen and it increases linearly with pressure. This equation was a good fit to the data for ammonia synthesis using hydrogen (protium) and deuterium[72]. Apart from merely representing the data, further merit was claimed in that :

(a) at a given temperature and pressure, the rate constant k is the same for the H_2 and D_2 system and this should be so, since it represents a rate constant for the adsorption of nitrogen.

(b) at a given temperature, k is strictly proportional to total pressure in agreement with its physical meaning.

(c) both k and a depend exponentially on temperature. Contrary to expectation the constant a was found to be independent of the pressure.

King[65] has criticized this treatment as the concept of P_N^* is not used. He argues that P_N^* is the pressure of nitrogen that would be in equilibrium with N_a. If this is incorporated the constant α has a value of 2. This would be meaningless since then $(1-\alpha)$, the coefficient in the decomposition rate equation, would be meaninglessly negative.

Further the value of $\alpha = 1$ found by Ozacki et al[72] is not reasonable since the decomposition reaction would be zero order which is not in agreement with experimental findings.

The third assumption of Temkin and Pyzhev[67] that nitrogen adsorption is independent of the presence of hydrogen or ammonia was not upheld by experiment. It has been shown[73,74,75] that the presence of hydrogen increased the rate of nitrogen uptake and the factor by which this is increased is linearly related to the amount of hydrogen adsorbed. Thus, although on separate catalysts the rate of nitrogen uptake in the absence of hydrogen was approximately equal to the rate of ammonia synthesis, under catalytic conditions nitrogen uptake was much faster. Hence we must either dismiss the rate of nitrogen chemisorption as the rate determining step in favour of one of the hydrogenation steps or otherwise assume that only a fraction of the nitrogen adsorbed is active in the reaction.

It was further found[75] and has been confirmed recently[78] that the total amount of hydrogen and nitrogen chemisorbed at equilibrium are mutually enhanced by the presence of each other. Although he originally found no isotopic effect[75] of hydrogen in the simultaneous adsorption of hydrogen and nitrogen, Tamaru[76] has now found that the reaction of chemisorbed nitrogen with deuterium proceeds faster than with hydrogen (i.e. protium). The isotope effects in the overall reaction[72] is thus attributed to the effect in the reaction between chemisorbed nitrogen and

hydrogen. Azuma[161] has observed by F.E.M. that the presence of presorbed hydrogen on tungsten greatly accelerated the rate of dissociative nitrogen adsorption. A similar effect was observed by Krasil'schikov and Antonova[163]. From these considerations it thus appears[77] that the hydrogenation of nitrogen is a step participating in the rate determining step of the overall reaction.

1.4.3. Application to decomposition experiments

The Temkin theory predicts the rate of decomposition should obey the equation

$$\frac{-dp_{NH_3}}{dt} = K \frac{p_{NH_3}^{2}}{p_{H_2}^{3}}^{m}$$

Experimental results are expressed as

$$\frac{-dp_{NH_3}}{dt} = K \frac{p_{NH_3}^{x}}{p_{H_2}^{y}}$$

According to Temkin's theory the ratio y/x should be 1.5. The value of x and y found by various investigators are listed in Table 1.3. In the table, taken in part from Bond[36] activation energies ΔE for decomposition are also listed. Temkin's theory is based on the desorption of nitrogen as the rate determining step and one assumption is that the adsorption of nitrogen is not influenced by the presence of hydrogen (vide infra). Hence, if hydrogen atoms are able to compete with nitrogen atoms on a particular metal the indices y would be increased leading to a value of y/x greater than

(contd. p.39)

Table 1.3

Kinetics of Ammonia Decomposition

Catalyst	x	y	y/x	Pressure range (torr)	E kcal/mole	Temperature range (°C)	Ref.
*W(w)	0	0.2	-	16-265	45.3	800-1000	6
W(f)	-	-	-	10- 53	38	385- 500	22
Mo(w)	0	0.5	-	~100	42.7	725- 850	6
Re(p)	.53	0.89	1.68	-	32.2	380- 440	59
Re(f)	.7	1.4	2.00	10- 53	49	455-570	22
Ru(s)	1.0	1.75	1.75	-	59.2	552- 736	70
Ru(a)	.6	0.91	1.52	600-800	30.5	340- 450	79
Ru(f)	1.2	2.0	1.67	10- 52	45	270- 465	22
Os(p)	0	1	-	50-300	47.6	290- 370	80
Os(s)	1	1.5	1.5	~ 760	~40	450- 600	71
Co(f)	0.85	1.42	1.67	10- 53	45.0	370- 480	22
Co(p)	-	-	-	-	53	580- 640	174
Rh(a)	0.6	-	-	300-500	25.9→31.1#	360- 450	79
Rh(f)	1.35	2.45	1.82	10- 50	57	420- 500	22
Pd(a)	-	-	-	300-400	27.8-32.1#	510- 570	79
Ni	-	-	-	-	52	580- 650	174
Zr	-	-	-	-	63	590- 670	174
Pt(w)	1	1	1	100-200	140	933-1215	4
Pt(r)	1	1	1	20- 76	-	1050-1160	81
Pt(w)	1	1	1	0.24- 4	44	1100-1485	82
Pt(w)	1.4	2.3	1.64	10-300	140	1100-1485	82
Pt(w)	1	0	-	~ 0.01	5.1	900-1357	83
Pt(w)	1.5	2.2	1.47	~ 0.01	49.3	474- 564	83
Pt(f)	0.96	1.63	1.70	10- 53	59	520- 610	22
Pt( )	1.0	1.5	1.5	-	-	-	70
Cu(p)	~1	~1	~1	~760	46.0	495- 620	14
Cu(p)	-	-	-	-	58-62	720- 910	175
Cu(p)	-	-	-	-	47	-	176

Catalyst	x	y	y/x	Pressure range(torr)	E kcal/mole	Temperature range (°C)	Ref
Cu(p)	-	-	-	-	44	620- 680	174
Fe(f)	0.5	0.7	1.4	10- 53	38.8	355- 470	21 22
Fe(g)	0.8	0.9	1.1	~760	-	-	12
Fe(a)	0.9	1.5	1.7	~760	54.0	492- 524	12
Fe(d)	0.6	0.85	1.4	-	45.2	335- 430	84
Fe(d)	-	-	-	-	59	400- 450	2
Fe( )	1.0	1.5	1.5	-	-	-	68

(a) = on Al_2O_3;

(d) = doubly promoted;

(f) = film;

(g) = gauze;

(r) = ribbon;

(s) = on SiO_2;

(w) = wire

* see also Table 1.1

≠ E increased with increasing P_{H_2}

1.5. The behaviour of ruthenium is attributed[70] to the strange adsorption of hydrogen on the metal. On the basis of the Temkin theory the measured activation energy E of decomposition can be expressed[61] as

$$E = E_d^o + \frac{x}{2}(\theta - q_o) \qquad 1.4.16.$$

where E_d^o is the activation energy for the desorption of nitrogen and q_o the heat of adsorption, both on a clean surface and θ is the heat of decomposition of two moles of ammonia. The constant x, the ammonia index, is also related to the way in which the activation energy for desorption and the heat of adsorption of nitrogen vary with coverage. Although Q is known[85] to be 25.4 kcal/mole, other terms in this equation are unknown for most metals.

There seems to be a symbatic relationship between x and E, i.e. if a catalyst has a low ammonia index it will generally have a low activation energy, and the corollary applies especially of $y/x > 1.5$. This is illustrated by selecting from Table 1.3 the following results.

Metal	x	x/y	E	Ref,
Re	0.53	-	32	59
Ru	0.6	-	30.5	79
Rh	0.6	-	30	79
Fe	0.5	-	38.8	21, 22
Ru	1.0	1.75	59.2	70
Ru	1.2	1.7	45	22
Re	0.7	2.0	49	22
Pt	0.96	1.7	59	22
Rh	1.35	1.81	57	22

It appears that for metals having $y/x = 1.5$, q_o is less than Ø if E_d^o can be considered constant for different species of any given metal. Where (y/x) is high equation 1.4.16 is not strictly applicable as there will be an additional contribution to E of part or all of the heat of adsorption of hydrogen which is inhibiting the reaction. Kemball[22] has evaluated $(E_d^o - \frac{x}{2} q_o)$ for his results :

Ni	Co	Ru	Fe	Rh	Rt	Re
31	34	30	32	40	46	41

showing the influence of (y/x).

Artyukh et al[174] have modified the Temkin-Pyzher equation for a mean nitrogen coverage of 0.5. This equation gave a good description of the kinetics on Co, Cu and Ni (67a). These have shown that the specific activity of a catalyst is dependent upon the "weight" of the d-state and the population of the d-orbital; that is the specific activity reflects the structure of the electronic orbitals and crystallographic lattices. The heats of activation for ammonia decomposition were not constant for all catalysts. This is not in agreement with the suggestion of Temkin and Kiperman[67a] and of Rusor and Pevzner[175] that the heat of activation should be independent of the chemical nature of the catalyst. Using a single crystal Voelter and Schoen[177] have also shown that the activation energy is a property of electronic geometric states of the catalyst for on the 111 plane it was 35 kcal/mole while on the 100 face it was 77.5 kcal/mole.

1.5. The Concept of Stoichiometric Number

A fresh approach to the problem of the mechanism of ammonia synthesis was devised by Horiuti[86-90] when he introduced the concept of stoichiometric number.

The formation of ammonia from its constituents takes place according to the stoichiometric equation

$$N_2 + 2H_2 \longrightarrow NH_3 \qquad 1.5.1.$$

Its synthesis on the surface of a catalyst will be a step-wise process with some of the steps occurring more than once. A given step (s) will be repeated ν_s times; ν_s is termed the stoichiometer in number of that step.

The suggested steps together with their stoichiometric numbers are :

		ν_s	
N_2 (g)	$\longrightarrow 2N$	1	1.5.2.
H_2 (g)	$\longrightarrow 2H$	3	1.5.3.
$N + H$	$\longrightarrow NH$	2	1.5.4.
$NH + H$	$\longrightarrow NH_2$	2	1.5.5.
$NH_2 + H$	$\longrightarrow NH_3$ (g)	2	1.5.6.

the subscript (g) refers to gas phase species, all other species are adsorbed.

To each step (s) we may assign a forward reaction rate $\overrightarrow{V_s}$ and back reaction rate $\overleftarrow{V_s}$. From statistical mechanics we know that the Gibbs free energy change for each step will be given by

$$\Delta F_s = -\frac{1}{RT} \ln \left(\frac{\overrightarrow{V_s}}{\overleftarrow{V_s}} \right) \qquad 1.5.7.$$

Thus the free energy change of the overall reaction is

$$\Delta F = \sum_{s=1}^{s} \nu_s \Delta F_s \qquad 1.5.8.$$

But the basic assumption in the ammonia synthesis reaction is that one step (r) is rate determining and all others are in equilibrium. Hence, except when s = r, $\overrightarrow{V_s} = \overleftarrow{V_s}$ and eqn 1.5.8 reduces to

$$\Delta F = \nu_r \Delta F_r = \frac{1}{RT} \ln \left(\frac{\overrightarrow{V_r}}{\overleftarrow{V_r}} \right) \qquad 1.5.9.$$

If the forward and back reaction rates of the overall reaction are $\overrightarrow{r}$ and $\overleftarrow{r}$ respectively then

$$\left.\begin{aligned} \nu_r \overrightarrow{V_r} &= \overrightarrow{r} \\ \text{and} \quad \nu_r \overleftarrow{V_r} &= \overleftarrow{r} \end{aligned}\right\} \qquad 1.5.10.$$

Therefore :

$$\frac{\overrightarrow{V_r}}{\overleftarrow{V_r}} = \frac{\overrightarrow{r}}{\overleftarrow{r}} \qquad 1.5.11.$$

Substitute of 1.5.11 into 1.5.9 gives

$$\ln \frac{\overrightarrow{r}}{\overleftarrow{r}} = \frac{-\Delta F}{\nu_r RT} \qquad 1.5.11$$

The equilibrium constant K_e of the overall reaction will be

$$K_e = A \exp \left[\frac{-\Delta F}{RT} \right] \qquad 1.5.12$$

where A is the classical activity term. It follows therefore that :

$$\frac{\overrightarrow{r}}{\overleftarrow{r}} = (K_e A)^{1/\nu_r} \qquad 1.5.13.$$

The rate (r) at which the overall reaction proceeds will be $(\overrightarrow{r} - \overleftarrow{r})$ and thus

$$r = \overrightarrow{r} \left\{ 1 - (KA)^{1/\nu_r} \right\} \qquad 1.5.14.$$

As the overall reaction is 1.5.1

$$A = \frac{P_N P_H^3}{P_A^2} \text{ and } K_e = \frac{P_N^e (P_H^e)^3}{(P_A^e)^2}$$

consequently (from 1.5.14)

$$r = \vec{r} \left\{ 1 - \left(\frac{P_A}{P_A^e} \right)^{2/\nu_r} \right\} \qquad 1.5.15$$

At a state close to equilibrium $P_A - P_A^e$ is small and $\vec{r} \simeq \vec{r}_e$.

This condition reduces 1.5.15 to

$$r = \frac{2\vec{r}_e}{\nu_r P_A^e} (P_A - P_A^e) = \frac{dP_A}{dt} \qquad 1.5.16$$

Integration of the last equation gives

$$\ln (|P_A^e - P_A|) = \frac{2\vec{r}_e}{\nu_r P_A^e} t + \text{const.} \qquad 1.5.17$$

For synthesis $P_A^e > P_A$, for decomposition $P_A > P_A^e$.

A plot of $\ln (P_A^e - P)$ against t in a closed system should give a straight line of slope $2\vec{r}_e/\nu_r P_A^e$. This allows ν_r to be calculated since $\vec{r}_e$ can be determined by isotope exchange $N^{15}/N^{14}H_3$ and P_A^e is readily found.

Horiuti[91,92] has found $\nu_r = 2$ for ammonia synthesis over doubly promoted iron catalysts. This would mean that one of hydrogenation steps was rate determining. This conclusion is in contradiction to the generally held opinion.

The expression (1.5.17) was derived assuming that all the steps except the rate determining one were in equilibrium. Furthermore in evaluating ν_r from the slope of $\ln (P_A^e - P_A)$ is t

a value of $\overrightarrow{r_e}$ was used which was obtained from $N^{15}/N^{14}H_3$ exchange experiment. It is thus assumed that :-

(a) exchange takes place only according to :

$$N^{15}N^{15} + N^{14}H_3 \rightleftharpoons N^{15}H_3 + N^{14}N^{15}.$$

(b) there is no isotope effect between N^{15} and N^{14} giving a false value of $\overrightarrow{r_e}$.

The first assumption has been examined by Enomoto and Horiuti[91] who point out that if any other reactions caused exchange the deduced value of ν_r would be too high. However, such a reaction seems unlikely.

Bokhoven et al[96] determined $_r$ over singly and doubly promoted iron. They measured r and $\overrightarrow{r_e}$ simultaneously and in a second experiment compared the ammonia synthesis rate with the rate of exchange of

$$N_2^{30} + N_2^{28} \rightleftharpoons 2N^{29}$$

in a mixture of N_2, H_2 and NH_3 having nearly equilibrium composition. The value of ν_r so obtained was 1, in agreement with the concept that the rate determining step is the chemisorption of nitrogen. This result has been criticised by the Japanese school[93,94]. These authors have shown that ν_r is extremely sensitive to the chosen value of P_A^e. As Bokhoven et al[96] obtained this value by approaching equilibrium from the direction of synthesis their value of P_A^e is probably lower than Horiuti et al[91,92] who calculated it by approaching equilibrium from both sides. Furthermore Bokhoven et al[96] used the rate equation of Temkin

and Pyzhev to exclude the stoichiometric number from rate of isotope exchange N^{15}/N^{14} and the rate "constant" has been shown to be dependent on the flow ratio[94]. Horiuti et al have re-examined Bokhoven's results and found $\nu_r = 2$.

In reply Bokhoven et al[97] claimed justification for their value of P_A^e because they had not reported a slight temperature difference between experiments. They had found their values were in good agreement with Haber's formula[98] for the equilibrium constant. However Haber's formula has an accuracy not better than 1%, indeed, even Gillespie and Beattie's[99] equation would have been accurate enough. Horiuti et al[95] have partly based their vindication of $\nu_r = 2$ on the fact that it gave a better constancy for k_s.

Thus although the stoichiometric number concept is a very promising one, its accurate experimental determination is not easy.

1.6. Surface Electrical Properties

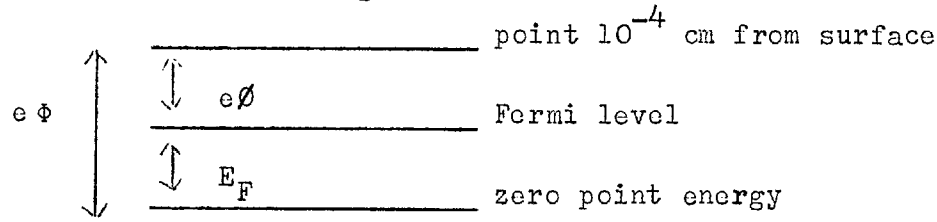
1.6.1. Definitions

The modern theory of metals visualises a metal as an array of positive ions between which exist the valence electrons. These electrons are distributed between various energy levels in accordance with Fermi-Divac statistics. The highest occupied energy level is termed the Fermi level and it is temperature dependent. The work function ϕ of a metal is defined as the energy difference between an electron in the Fermi level and one at rest 10^{-4} cm from the surface, this distance is chosen as experiment has indicated

that at a distance greater than 10^{-5} cm from the surface the classical mirror image force, $q^2/4x^2$, is negligible. At this point an electron has a potential energy $e\Phi$ while an electron in the Fermi level has kinetic energy E_F. If the electrostatic potential difference between these points is $\emptyset$ volts, we may write

$$e\emptyset = e\Phi - E_F$$

e being the electronic charge.



The potential difference W is complicated by the presence of a double layer at the surface of the metal. The discontinuous nature of the surface gives rise to an unsymmetrical distribution of the electrons with respect to the positive ions and hence a double layer of positive and negative charge is formed. If these are σ charges per unit area and the double layer has a thickness d then the dipole per unit area, σd, sets up a potential difference of $4\pi\sigma d$ which is the surface potential, χ. If the electrostatic potential just inside and outside the metal are Φ_{inner} and Φ_{outer} respectively.

$$\chi = \Phi_{outer} - \Phi_{inner} = 4\pi\sigma d.$$

The thermodynamic basis of the work function has been reviewed by Herrings and Nichols[100,101,102]. The electrochemical potential $\bar{\mu}$ of an isolated body of volume V, containing n electrons is defined as

$$\bar{\mu} = \left(\frac{\partial F}{\partial n}\right)_{T,V}.$$

where F is the Helmboltz free energy $F = U - TS$. Thus $\bar{\mu}$ is identifiable with E_F, the Fermi level. The electrostatic potential Φ of the body is not invariant and can be altered by moving external charges etc. To isolate the effect of charge distribution on surface conditions we define the chemical potential μ as

$$\mu = \bar{\mu} + e\,\Phi_{inner} \qquad (a)$$

But the work function ϕ is

$$\phi = -\Phi_{outer} - \frac{\bar{\mu}}{e} \qquad (b)$$

and the surface potential χ is

$$\chi = \Phi_{outer} - \Phi_{inner} \qquad (c)$$

Equations (a), (b) and (c) give

$$\phi = \chi - \frac{\mu}{e}$$

The parameter μ/e is termed the "inner work function" and is a property of the material only. It generally accounts for about 80% of the work function[103]. The surface potential is a structure sensitive property and χ will have a different value for each crystal face of a metal. Hemce the work function ϕ will change from face to face; this is a well established fact (for example[104] and [105]).

The contact potential difference, C.P.D., the basis of which has been reviewed by Chalmers[106] and Koenig and Lange[107], is now defined. If two isolated and electrically neutral conductors (A and B) are placed in electrical contact electron transfer occurs until $\bar{\mu}_A = \bar{\mu}_B$. Since

$$\phi = \Phi_{outer} - \frac{\bar{\mu}}{e}$$

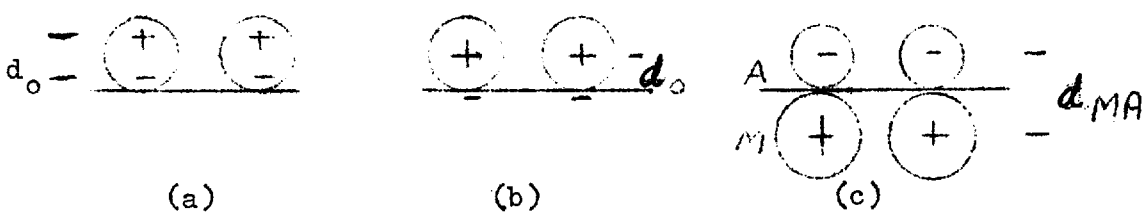
at equilibrium $V_{AB} = (\Phi_A - \Phi_B)_{outer} = \phi_B - \phi_A$ where V_{AB} is the volt or con stant potential difference.

1.6.2. Modification of surface properties by adsorption

When a gas is adsorbed on a metal surface electronic interaction between the adsorbate and adsorbent give rise to a change in the work function of the metal. The effect is assignable to a change in the dipole layer at the surface. The σ dipoles per unit area aligned perpendicularly to the surface approximate to a double charge layer. The positive and negative charges, of density σ, are separated by a distance d. If co-operative effects are ignored the system may be regarded as a capacitor, the potential of which is proportional to the number of individual dipoles per unit area. The dipole moment M = ed. As there is no field associated with a perfect double layer, the electrostatic potential changes sharply by $\pm 4\pi\sigma M$ in moving across the doublellayer. As the inner work function, μ/e, in a bulk property unaltered by adsorption the total work function is altered by $\pm 4\pi\sigma M$ or $\Delta\phi = 4\pi\sigma_m\phi$ where $\sigma = \theta\sigma_m$, σ_m being the total number of sites per cm^2 available to the adsorbate and θ the fraction of these occupied. The change $4\pi\sigma_m\theta$ in ϕ caused by adsorption is actually a change in the surface potential. It is conventional to speak of this change in the surface potential of the metal M by adsorption of gas G as the "surface potential of G on M". This change $\Delta\chi$ is equal in magnitude but of opposite sign to the work function change but is expressed in volts not eV.

It has been shown that the C.P.D. between two metals in electrical contact is given by $V_{AB} = \phi_A - \phi_B$. If adsorption occurs on metal A its work function changes from ϕ_A to ϕ_A' and there will be a corresponding change in the C.P.D. for V_{AB} to V_{AB}'. As $\Delta V_{AB} = \Delta\phi_A = 4\pi\sigma M$ a change in C.P.D. can be related to a change in S.P. of the metal performing adsorption. The second metal, B, if a reference electrode which should not take part in the adsorption process.

Surface potential measurements are undertaken to obtain information on the nature of the surface bond. Surface dipole moments are inaccessible as the charge separation distance is never known precisely. The dipole moment resulting from adsorption will depend upon the type of interaction.



(a) (b) (c)

(a) van der Waals' adsorption

The physically adsorbed molecules are held to the surface by weak dispersion forces and are slightly polarized by the surface field. Alternatively there may be slight charge transfer. In either case the resulting dipole M is small and will have its positive side outward. The surface potential change is $\Delta\phi = 4\pi\sigma_m \Theta M$, where M = edp.

(b) Ionic adsorption

Langmuir[108] considered the double layer formed on a conducting surface by a completely ionized adsorbate to be formed by adions and their electric image in the metal. Electrons emitted from the surface would cross only half the double layer and hence $\Delta\phi = 2\pi\sigma_m \Theta M$ where M = ed, where d is the distance between the charge and its image. The reality of these image charges has been questioned[109] and the theory of image forces shows the charge is almost entirely on the surface opposite the adatom[110]. The effective dipole length is then d_o (see fig.1.10.b)

thus $M = ed_o$ and

$$\Delta\phi = 4\pi\sigma_m \Theta M.$$

This type of adsorption can result in positive or negative surface potentials depending upon the polarity of the adion formed.

(c) Covalent adsorption

If it is assumed that effective metallic conduction begins at the metal surface the effective dipole length is $d_m A/2$ (fig.1.10.c) and $\Delta\phi = 2\pi\sigma_m \Theta M$. Covalent adsorption generally results in negative surface potentials but the sign naturally depends upon the direction of electron transfer.

The variation of surface potential with coverage is never linear as predicted by simple theory. The reason for this deviation has been extensively considered by Macdonald and Barlow[111].

1.6.3. Measurement of surface potentials

The change in surface potential can be evaluated by directly measuring the work function before and after adsorption, by measuring the C.P.D. between surface A and a reference surface, B, or by measuring some property dependent upon C.P.D. Generally the direct work function measurement such as photoelectric, thermionic or field emission methods give a work function average "weighted" in favour of a certain crystal plane while the other methods give a work function integrated over the surface. These methods have been comprehensively reviewed by Boudian[112], Mohring[113] and Culver and Tompkins[114].

Thermionic emission

A uniform surface of a material having a work function ϕ, at temperature T will give an electron flux, j, such that

$$j = A\ (1 - \bar{r})T^2 \exp\left[\frac{-e\phi}{kT}\right]$$

where $\bar{r}$ is the mean reflection coefficient of electrons at the surface, assuming a Maxwellian distribution and A is a constant. A plot of log j/T^2 against $1/T$ will give the "Richardson plot". Hence the work function and any change can be measured. The emission equation is valid for each of the patches on a non-uniform surface, but the total measured current from the various patches depends on the relative magnitudes of the collection and patch fields as well as the work function. Thus the average work function for a poly-crystalline surface measured thermionically may differ from the

true average work function. The method is limited to adsorbants having a work function low enough and a melting point high enough to allow a temperature high enough to give a significant emission. The high temperatures will generally cause desorption of the adsorbed layers. Becker[115] has described the use of this method.

Field Emission Microscope

The barrier to electron emission is modified by an external field F, volt/cm, at the surface and tunnelling probability is increased sufficiently to cause emission. The emission obeys the Fowler-Nordheim[116] equation.

$$j = V^2 \text{ ab exp } (-6.84 \times 10^7 \, \phi^{3/2} / kV)$$

where j is the total current, V the applied voltage, a the emitting area and $k = F/V$, the constant $b = 6.2 \times 10^6 \, k^2 \, (E_F/Q)^{1/2}(E_F + \phi)^{-1}$. The equation has been found to be obeyed[117] within the experimental uncertainty of F (15 - 20%). The work function which may be obtained from the slope of log (j/V^2) against V^{-1} or by direct use of the Fowler-Nordheim equation, are weighted in favour of those parts of the surface having high electron emission. The F.E.M. has been reviewed by Muller[118] and Cromer[119]. Recently Erhlich[47] has critically examined the use of the Fowler-Nordheim equation for obtaining work functions of adsorbed layers. The equation is based on a simple one dimensional image force potential and does not account for the presence of discrete atoms on the surface which alter the shape of the barrier through which the electrons tunnel nor for the consequential reduction in area.

It is suggested[47] that accurate work functions can be derived from the field dependence of the emission but not from the absolute current value at a fixed applied voltage as used by Becker[49]. The question of the barrier to electron emission has been extensively discussed recently[120].

The photoelectric method

When light of frequency ν falls on a surface photoelectrons are emitted having an energy of $h(\nu - \nu_o)$ where ν_o is the threshhold frequency. This energy is obtained by measuring a voltage V_3 sufficient to suppress emission.

Thus :

$$eV_3 = h(\nu - \nu_o)$$

The threshhold frequency is related to the work function by Einstein's equation $h\nu_o = e\phi$. This equation was derived for θ^oK but remains valid at room temperature. The work function before (1) and following (2) adsorption are thus related by :

$$\phi_1 - \phi_2 = h(\nu_{01} - \nu_{02})$$

As there is a tendency for patches having high work functions to be excluded the photoelectric work function will be lower than the true work function average. The method is limited by three main disadvantages :-

(i) photocurrents of the order of 10^{-14} A have to be measured accurately,

(ii) work functions greater than 5V require ultraviolet techniques,

(iii) at pressures greater than 10^{-4} torr gas ionization by collision occurs.

The method is exemplified by the techniques of Suhrmann and Sachtler[121].

The Magnetron method

The magnetron is a cylindrical diode with an axial magnet field which reduces the saturation emission current. Contact potential differences are measured between the clean and covered anode surface using a central tungsten cathode as a reference.

The total potential V between the electrodes is given by[122]:-

$$V = V_a + V_{AR} + V_t$$

where V_a is the applied potential, V_{AR} is the C.P.D. between anode and cathode, and V_t is a temperature dependent term related to the kinetic energy of the emitted electrons. To reduce the anode current to half its original value a field strength of H_o is required and it has been shown[123] that

$$V = \frac{H_o^2 R^2 e}{8m}$$

where R is the radius of the anode, and e/m the charge to mass ratio of the electron. Thus $V_a + V_{AR} + V_e = kI_o^2$

where k is a constant depending upon the geometry of the diode. When I_o^2 is plotted against V_a the intercept is $-(V_{AR} + V_t)$ whence V_{AR} may be found if V_t is known.

This method has been used by Wilson and Weissler[124]. It cannot be used at a pressure above 10^{-4} torr since the electrons collide with the gas. A further disadvantage is the practical one of outgassing the comparatively large metal parts without disturbing

their geometry upon which the accuracy of the method depends.

The vibrating capacitor

As shown above if two conductors A and B at the same temperature are connected by a circuit having no e.m.f. source their would be a potential difference given by $V_{AB} = \phi_A - \phi_B$. In this method one of the plates is vibrated and an a.c. signal is produced and amplified. A potential V, of opposite sign to V_{AB}, is applied to the plates and increased until the a.c. signal is removed, at which point $|V| = |V_{AB}|$. This is done with a clean surface and a surface covered with an adsorbed layer to give the surface potential. This requires one of the plates to be inert towards the adsorbate; to this end oxidized Ni and Pt have been used[126].

This method was first used by Zisman[125] and has been skilfully developed by Mignolet[127-129]. A slightly different approach[105] has been used to measure the C.P.D. of germanium crystal faces. Pratt and Kohn[130] have produced an excellent modification of this method in which the vibrating plate is replaced by a disc which rotates eccentrically across the adsorbent surface. As this produces a greater periodic change in the capacity the method is more sensitive than the vibrating method and can measure changes of 1 mV.

The static capacitor

Eberhagen[132] devised a new capacitor method in which the plates are stationary. This method has been successfully developed by Delchar[133]. When adsorption takes place on one plate the

equilibrium $\bar{\mu}_A = \bar{\mu}_B$ is upset since $\bar{\mu}_A$ is changed by the adsorption process. This results in a flow of charge (in an external circuit) to regain equivalence of Fermi levels. The electron flow is detected by a sensitive d.c. amplifier which operates a servo-mechanism. This applies to the plates a potential of sign and magnitude just sufficient to balance the change in C.P.D. This potential was recorded automatically. The time lag between adsorption and compensation was approximately 150 millisecs. and the change in C.P.D. was consequently slightly low but this increment could be calculated.

Space charge limited diode

The maximum electron flux which can be drawn from the cathode of a diode is given by the Richardson equation (vide supera). If the current density is low electrons emitted from the cathode build up an electron atmosphere or "space charge" around the anode. This space charge presents an electrostatic barrier to electrons flowing to the anode. This barrier is higher than the anode surface barrier, which comprises the work function plus the Fermi inner potential energy. Hence the current is controlled by the space charge, which is a function only of temperature. Crysae and Wagner[134] have shown on a basis of a Maxwellian distribution of electron velocities, that the current flowing between the anode and cathode depends almost entirely on the applied voltage and the mean anode work function. Thus a shift in the current/voltage characteristic due to a change at the anode surfaces represents the change of anode work function.

In the diode the cathode is generally a tungsten filament maintained as a reference electrode at a temperature above which adsorption occurs. The anode may be a wire[e.g.135], ribbon[e.g.136] or evaporated metal film[139etc]. To evaluate a S.P. the i/v curve is first obtained for a clean anode surface A and then for an anode with adsorbed gas A'. The displacement gives the S.P.

Fig. 1.11 deflection

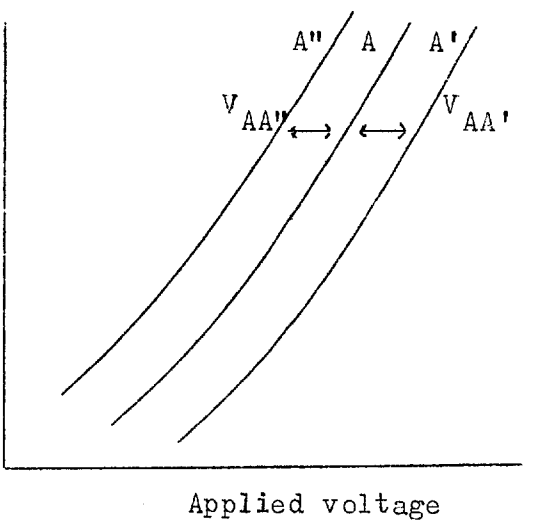


Figure 1.11 shows A the i/v plot for a clean surface. Curve A' and A" are for an anode whose work function has been increased and decreased respectively i.e. $V_{A'A}$ represents a negative S.P. and $V_{A"A}$ a positive S.P. As this method is that used in the present work further practical details are given in Chapter 2. It has the following disadvantages :

(a) it cannot be used with an ambient pressure in excess of 10^{-4} torr for the electron/gas collisions destroy the parallel nature of the plots,

(b) the hot tungsten emitter may have a disrupting effect on some gases; however, this can be useful, i.e. in studying hydrogen atom adsorption[e.g.140].

This method, initiated by Bosworth and Rideal[135], has been used by Mignoll[127,128,129etc], Tompkins et al[140,141etc] and others.

The application of these methods and the information obtainable for S.P. measurements have been comprehensively reviewed by Tompkins[114] and Eberhagen[131].

1.6.4. The surface potentials of H_2 on metals

The surface potentials of hydrogen on various metals are listed in table 1.4. The S.P. on tungsten, the metal in which the present work is most interested, is well established. The value of Bosworth and Rideal[135] may be ignored for although much credit must go to them for developing the crossed filament diode method the nascent state of vacuum technology at that time did not make for accurate S.P. measurement. The question of clear metal surfaces is discounted by Culver and Tompkin[114]. Surface potential measurement on different crystallographic faces of tungsten by F.E.M. methods[142] have shown that a number of hydrogen species can exist. As only some faces were able to show a multiplicity of adsorbed species, these results can be explained in terms of *a priori* heterogeneity for these faces only had sites of differing adsorption potentials.

To explain the observation[3] of two types of hydrogen adsorption on iron catalysts it has been suggested[2] that hydrogen can exist polarized with either a negative or positive charge outward.

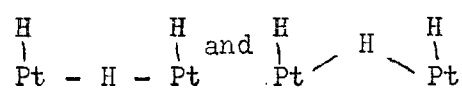
Table 1.4

Surface Potential of Hydrogen on Metals

Metal	S.P.(volts)	Method	Ref.
Fe	-0.19	Photoelectric	169
	-0.43	Diode	160
	-0.47	Capacitor	109
Co	-0.33	Diode	126
Ni	-0.1	Photoelectric	158
	-0.12	Photoelectric	169
	-0.35	Capacitor	126
	-0.35	Diode	160
	-0.39	Photoelectric	154
	-0.40	Capacitor	170
	~ -0.5	F.E.M.	171
	0.35	Static condenser	133
Cu	0.33	Diode	172
	0.36	Diode	160
Ag	0.34	Diode	160
	0.49	Capacitor	170
Au	0.18	Diode	160
W	-0.48, -0.65	Capacitor)	139,127
	-0.50	Diode)	128,129
	~-0.55	F.E.M.	173
	-1.04,-1.26	Diode	166
Ta	-0.44	Photoelectric	158
	-0.43	Photoelectric.	169
Pt	-0.14	Capacitor	144
	-0.15	Diode	144

As the latter would be the more stable at higher temperature this would be important in ammonia synthesis. Surface potential measurements[143] of adsorbed hydrogen, carbon monoxide and mixtures thereof on nickel films have shown two types of hydrogen adsorption. The weakly bound, and therefore reactive species, is formed between two adjacent metal atoms. Whereas earlier investigators had considered the non-linearity in surface potential/coverage curves to result from co-operative effects, Mignolet suggested[126,127] that this might reflect the existence of more than one type of chemisorption. Thus in the Pt/H_2 system[144] the initially S.P. is negative but eventually a positive layer is formed. This is too extreme for the answer to be in mutual dipolarization.

The suggestion[114] that the final stages are due to a weak molecular chemisorption was proved incorrect by the I.R. experiments of Pliskin and Eischene[145]. These authors suggested two possible structures :



in which there are two different topographical positions for hydrogen, considered to be held interstitially about 1Å from the surface between two CO molecules held on adjacent metal atoms. It has a positive charge of approximately half an electronic charge on the exterior. The second species is found on free metal atom sites and is strongly bound with a dipole negative outwards. The existence of "protonic hydrogen", the first species, was confirmed by S.P.

measurement with oxygen and hydrogen[146]. Tompkins[147] considers this to be the active species in ammonia synthesis where adjacent metal atoms are occupied by adsorbed N-containing species.

As the electron transfer process of chemisorption changes the charge carrier density in a metal[148], resistance changes of thin films resulting from adsorption are observed[149]. It has been suggested that the result of such experiments with Ni/H_2[150,151,152] and Fe/H_2[153] confirms the existence of two species. Mizushima[168] has gone so far as to claim that his results show three hydrogen species on nickel; (i) negatively charged atoms, (ii) postively charged atoms and (iii) molecular hydrogen.

1.6.5. Surface potential of nitrogen on metals

Tungsten

Bosworth and Rideal[135] reported the surface potential of nitrogen on tungsten wire as -1.38V. Mignolet[139] has re-measured the S.P. on an evaporated tungsten film using the vibrating condenser method[126] as -0.5V at 293°K. Using photoelectric methods, Suhrman[154] and Eisenger[155] obtained -0.22V and -1.0V respectively. It has been suggested[136] that high saturation adsorption on the 113 lattice of Eisenger's monocrystal produced the high value. Becker[156] using F.E.M. obtained -0.3V. Other workers have agreed with Mignolet, they obtained -0.54V at 300°C[136] using the crossed filament technique and -0.50V at 305°C from F.E.M.[45].

Recently, however, having taken precaution to getter the nitrogen with a nickel film, Ehrlich[47] measured the S.P. as

+0.1V. It was pointed out that, because oxygen, carbon monoxide and hydrogen have effects on the surface potential that are large by comparison with that of nitrogen, such gases present in even a minute amount would greatly influence the recorded surface potential. On a consideration of respective adsorbing areas the F.E.M. method can clearly be seen to be more sensitive to small amounts of impurities than are methods involving films. Although high and low field techniques can give different S.P. values it was demonstrated that the change of sign was not so caused, for using ungettered nitrogen a S.P. of -0.5V was obtained. Pethica[137] also reported a positive S.P. when he made an alteration to his experimental technique. Redhead[157] has not been able to obtain such a change of sign and suggested the difference between the experiments was due to (a) different crystal planes exposed on a wire and a ribbon, or (b) contamination in Pethica's[137] experiment. Pethica[138] has discounted (b) but agrees with (a) and further adds that the disagreement may arise from the difference between measurement made with a space charge limited diode[137] and a retarding field diode[157]. Delchar[133] recorded a maximum S.P. of -0.2 while Azuma[161] obtained -0.55 in agreement with Mignolet[139]. Heating lowered the S.P. to -0.35 corresponding to a W ≡ N layer perhaps. The introduction of hydrogen caused a dramatic change in the field-ammonia current which was interpreted as hydrogen accelerating the dissociative adsorption of nitrogen. Azuma concluded that the rate-determining step in ammonia synthesis is not the dissociative adsorption of nitrogen but one of the hydrogenation steps.

Other metals

In table 1.5 are summarized the measured S.P. of nitrogen on various metal films other than tungsten.

Table 1.5

S.P. of N_2 on Metal other than W

Metal	Method	S.P.	Ref.	Temperature
Ta (crystal)	Photoelectric	-0.38	158	-
Cu	Condenser	+0.45	164	83°K
Ni	Condenser	+0.21	126	90°K
Ni	Diode	+0.23	141	90°K
Fe	Diode	-0.40 (at 130°C) +0.28 (at-185°C)	141	90°K

It appears likely that on Fe, Ni and Cu nitrogen is non-dissociatively adsorbed at temperature below 100°K. When a nickel film[141] exhibiting a S.P. of +0.23 at 90°K was heated to 195°K the S.P. decreased to 0.1V and about half the nitrogen was desorbed. At 25°C desorption was complete and the S.P. was zero. The heat of adsorption of nitrogen has been measured isosterically[165] and calorimetrically[41] and found to be ca. 10 Kcal/mole. Trapnell[167] has suggested that nitrogen is held molecularly with partial dissociation of the N ≡ N triple bond but Tompkins[141] does not exclude physical adsorption. Adsorption of nitrogen on iron gave a S.P. as θ curve which suggested the admolecules were mobile.. On warming to 20°C there was partial desorption followed by

re-adsorption and the S.P. became negative, -0.2V. A maximum value of -0.40 was obtained after heating for 10 hr at 130°C. These observations indicate molecular nitrogen was adsorbed at 90°K and this was transformed to a negative layer on warming. The desorption-adsorption process suggested that the surface dissociation (without desorption) received a higher activation energy than that of N_2 coming from the gas phase. The transition of molecules to atomic nitrogen was more clearly indicated when nitrogen was adsorbed on a clear film at 20°. Immediately after addition of each dose of N_2 at low coverage the S.P. momentarily increased and subsequently decreased to -0.02.

Krasilschikov and Antonova[163] have claimed their results, obtained using a silver-air electrode, indicated the existence of N_2^- on iron at 425°C.

1.6.6. The surface potential of ammonia on metals

There is very little data on the surface potential of ammonia adsorbed on metal. Gundry et al[141] have measured surface potential changes during the adsorption of ammonia, nitrogen and hydrogen on evaporated films of nickel and iron. On addition of ammonia to the system at -78°C there was initially no change of work function although, allowing for ammonia adsorption on glass[19], it appeared that ammonia had reached the film. This was explained by assuming the dipole moments of the amino radical and hydrogen atom were approximately equal but of opposite sign. Dissociation chemisorption was indicated by the fact that the large change in surface potential

ultimately obtained by further addition of ammonia increased with time (i.e. a slow and therefore activated process was occurring) and the adsorption was not reversible. The maximum surface potential was positive, 2.1 and 0.65V for nickel at -78°C and iron at 20°C respectively while in general a positive S.P. suggests physical adsorption but it is unlikely in this case and it was suggested that the positive potential resulted from an activated transformation of the H adatom from its interstitial surface site to one outside the surface between adjacent chemisorbed amino radicals with a change of sign and magnitude of its dipole. This was also observed with CO + H and O_2 + H_2 systems[143]. This H^+ species could account for the observation[20] that the NH_3/D_2 system exchange one hydrogen at a time.

Raising the temperature of the film to 20° caused little desorption but the S.P. became increasingly less positive, which could be explained in terms of further decomposition of the amino radical. If this were so the -NH radical so formed would have to have a dipole sufficiently more negative than the $-NH_2$ radical to override the extra protium hydrogen formed.

In an attempt to observe ammonia synthesis hydrogen was adsorbed on nickel which already had a nitrogen layer adsorbed on it and this caused a slight decrease in S.P. Warming to 20° removed the nitrogen (as in an experiment performed with nitrogen only) leaving a negative S.P. corresponding to partially covered atomic hydrogen layer. Thus there was no evidence for ammonia

formation at these comparatively low temperatures. With iron addition of hydrogen at 20°C to a film previously covered with nitrogen at 100°C with a surface potential of -0.25V, caused the S.P. to change to +0.07V; this drifted spontaneously to -0.04V indicating perhaps the formation and subsequent desorption of ammonia.

Azuma[161], using a field emission microscope, has measured surface potentials of nitrogen, hydrogen and ammonia on tungsten. He observed that adsorbed hydrogen atoms accelerated the rate dissociative adsorption of nitrogen. Ammonia did not give the characteristic pattern of nitrogen atom but that of hydrogen. On heating to 1700°K a positive surface potential species, $-NH_2$ or $\equiv NH$, was formed from a mixture of N_2 and H_2. He estimated the S.P. of ammonia on tungsten to be +0.1V at -78°C.

Krasil'schikov and Antonova[163] have measured the adsorption potential of H_2 and N_2 on Fe at 428°C using a silver-air electrode. The potential of an adsorbed H_2/N_2 mixture was more negative (i.e. had a positively charged dipole away from the surface) than that due to either gas adsorbed singly. This can be explained by the transformation of H^- to H^+ when neighbouring adsorbent atoms are nitrogen containing.

1.7. Summary

We have seen that in spite of much investigation the rate determining step is still an open question.

The Temkin-Pyzher theory, which is based on the assumption that the chemisorption of nitrogen is rate determining, has satisfactorily

described the kinetics of at least some of the experimental data. Adsorption rate and exchange rate measurements have shown that nitrogen adsorption proceeds at a rate comparable to the rate of ammonia synthesis. But Tamaru[75] has demonstrated that the rate of nitrogen uptake during ammonia synthesis is much greater than the rate of ammonia production. This has been further shown by S.P. studies[161,162]. Also, against the hypothesis of nitrogen chemisorption being rate determining, is the observation[72] that there is an H_2/D_2 isotope effect in ammonia synthesis.

The concept of stoichiometric number[86] has provoked much interest but has proved indecisive. The Japanese school claim $\nu_r = 2$ which implies the rate determining step is one of the hydrogenation steps. But Bokoven et al[96] have measured ν_r as 1, i.e. in favour of nitrogen adsorption.

King[65] has suggested the dilemma can be solved by postulating two adsorbed nitrogen species. We have seen that such is often the case. He shows that all values between 1 and 2 are accountable on this basis.

Tamaru[178] has suggested that there is no paradox and that the rate-determining step of the overall reaction depends upon the reaction conditions. At low temperature and high pressures it is the chemisorption of nitrogen and at higher temperatures and lower hydrogen pressure it is the hydrogenation of nitrogen.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

2.1.1. Gases

Ammonia was prepared by repeated low temperature distillation over sodium metal of commercial ammonia supplied by Imperial Chemical Industries. It was then stored in a vessel fitted with a small side arm by means of which the ammonia could be frozen out.

Hydrogen was obtained from British Oxygen Company and purified for each experiment by diffusion through an electrically heated palladium thimble.

Nitrogen was obtained from B.O.C. in sealed glass ampoules and was used without further purification. The specification was :-

nitrogen	99.998%
oxygen	less than 10 v.p.m.
carbon dioxide	less than 5 v.p.m.
hydrogen	less than 1 v.p.m.
argon	less than 5 v.p.m.

Carbon monoxide, oxygen and krypton were similarly obtained.

2.1.2. Metals

The majority of experiments were performed with tungsten films. These were evaporated from 0.01" (0.25 mm) diameter

wire which was kindly donated by the Osram Lamp Company. Mass spectrographic analysis showed an impurity content of Fe = 0.05% and Si = trace.

Copper films were thrown from commercial copper wire. Siddigi[179] has shown this is of adequate purity. Nickel, iron and molybdenum were supplied specroscopically pure by Johnson, Matthey & Co.Ltd.

2.2. Apparatus

The apparatus was constructed mainly of Pyrex glass; the glass/tungsten seals were of W.1. glass.

2.2.1. Pumping system

Evacuation was effected by a Jencon high speed mercury pump backed by a 2 stage Edwards' rotary oil pump. A dynamic vacuum of about 10^{-8} torr was obtained with this combination. The pumping speed of the conveniently compact Jencon pump was comparable to that of an earlier arrangement of a high speed "Klamperer" in series with a 3-stage umbrella jet pump.

2.2.2. Gas metering system

The adsorption system is shown in fig.2.1. The volume between a reference mark on C and the point of cut off of B was 1.86 cm^3. Gases were admitted via tap No.1 and the pressure in this volume was measured by manometer A. Pressures between 5 and 50 torr were measured. The mercury in B was raised to enclose the known volume of gas. When C was lowered the gas expanded into the storage bulb. With F raised to a reference level and E,

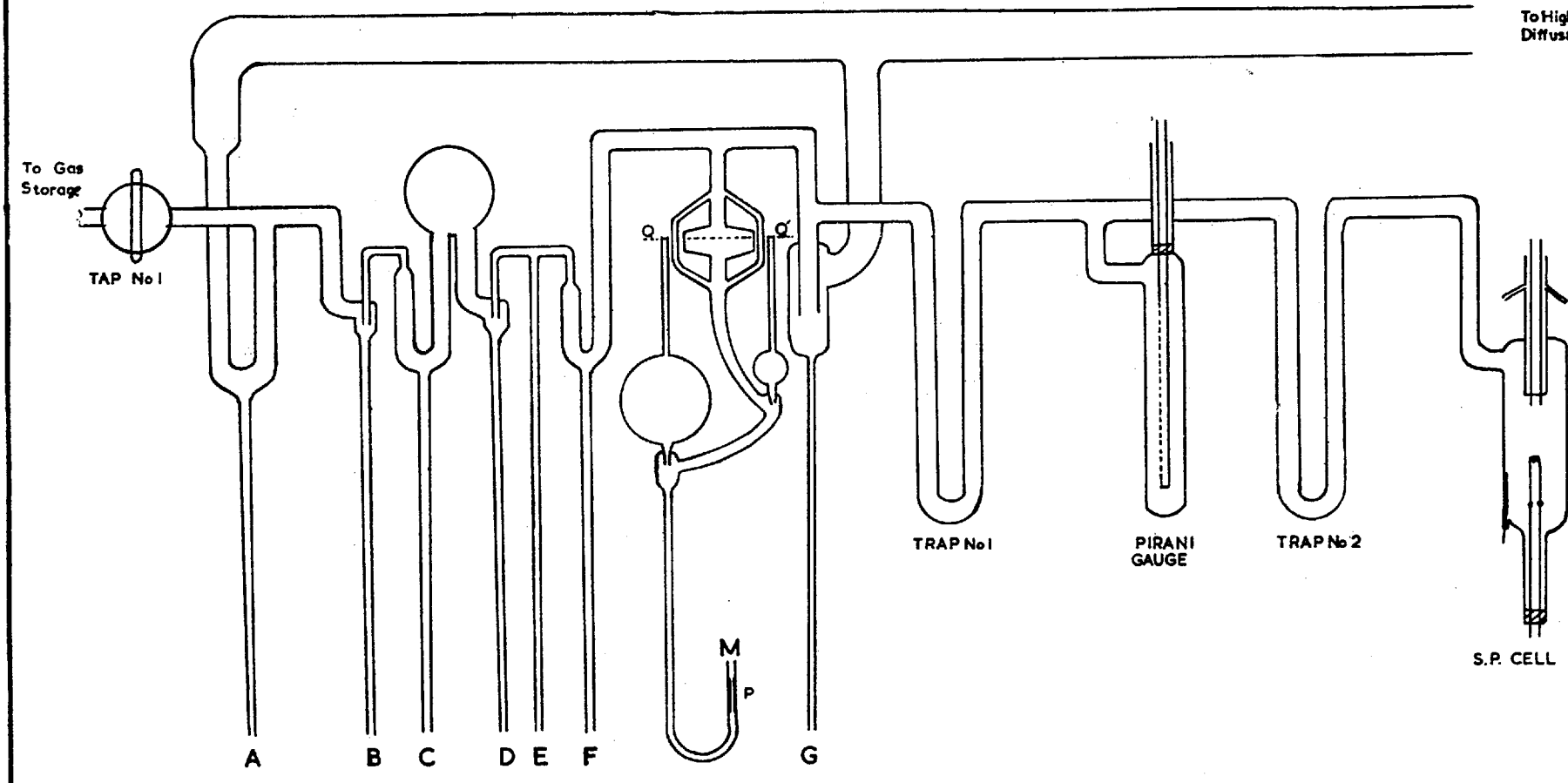


FIG 2·1 ADSORPTION SYSTEM

a gas burette, raised to one of two reference levels D was lowered and then raised to meter either 1.51% or 4.60% of the original dose. This was admitted to the cell through F.

2.2.3. Pressure measurements

The pressure in the system could be measured by both a McLeod gauge and a Pirani gauge. The McLeod was so constructed to permit rapid readings. Admission of air caused the carefully adjusted quantity of mercury in the reservoir to fall to a reference level P and correspondingly rise to QQ'. The ratio of the cross-sectional areas at Q and P was 1:300. Thus an atmospheric pressure variation of $\pm$ 3 cm gave a variation of $\pm$.1 mm at QQ'.

The Pirani gauge comprised a spiral "200V/40W" tungsten lamp filament (unflashed and uncoated) stretched between tungsten rods. At atmospheric temperature and pressure it had a resistance of 80 ohms. In operation the resistance of the Pirani filament was measured by a Wheatstone Bridge. The stabilized power supply to this bridge had an output of 40 mA at 300 V. The Pirani circuit is given in fig.2.2. The gauge was immersed in a bath at 195°K (i.e. solid CO_2/alcohol), the level of which was kept constant at a reference mark 3 cm above the upper-end of the filament.

2.2.4. The surface potential cell

The design of the surface potential cell was subject to slight modification as the work progressed. The final, most successful, design is shown in fig.2.3. The emitter filament (cathode) was

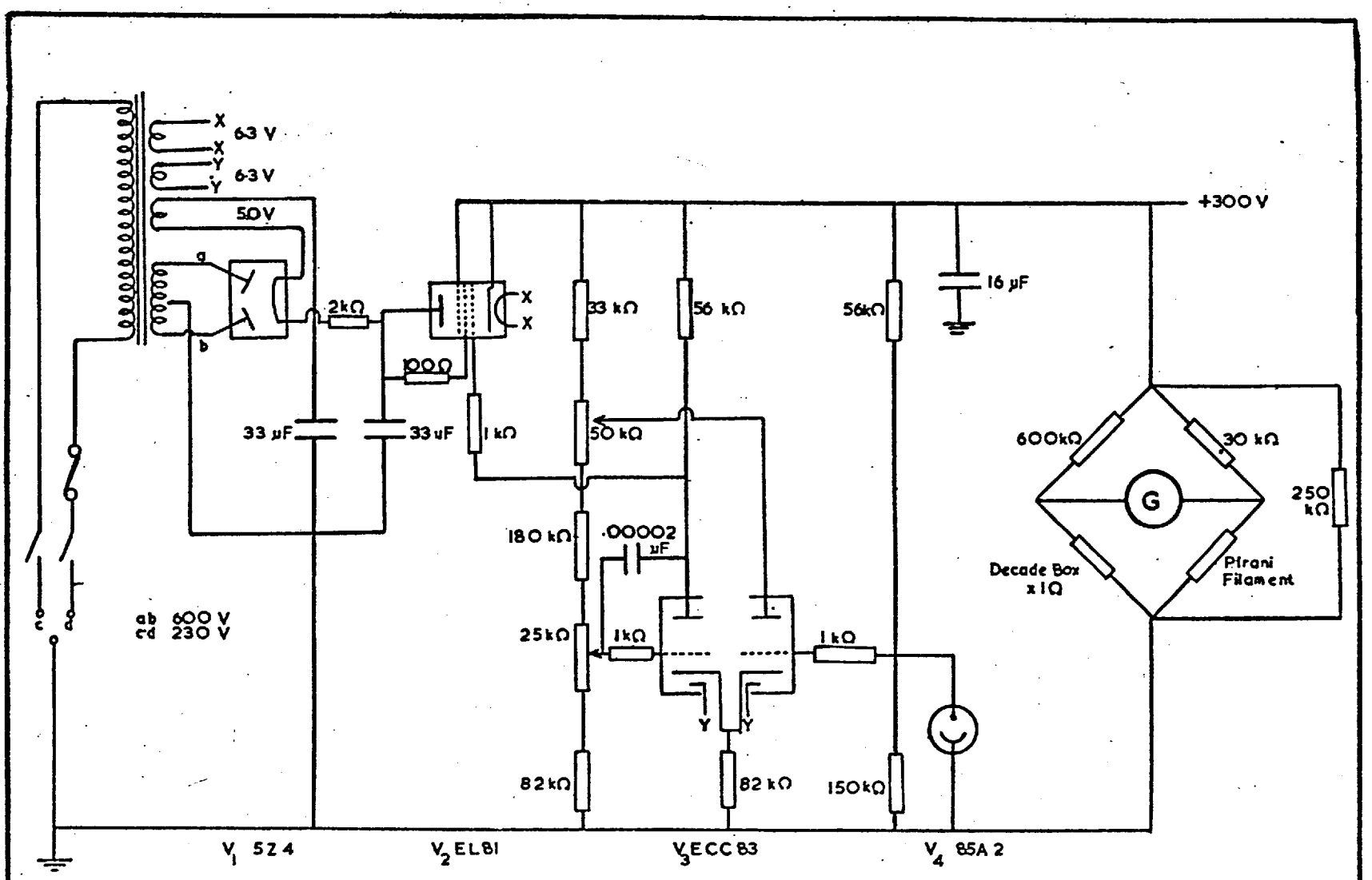


FIG 2·2 Pirani Circuit

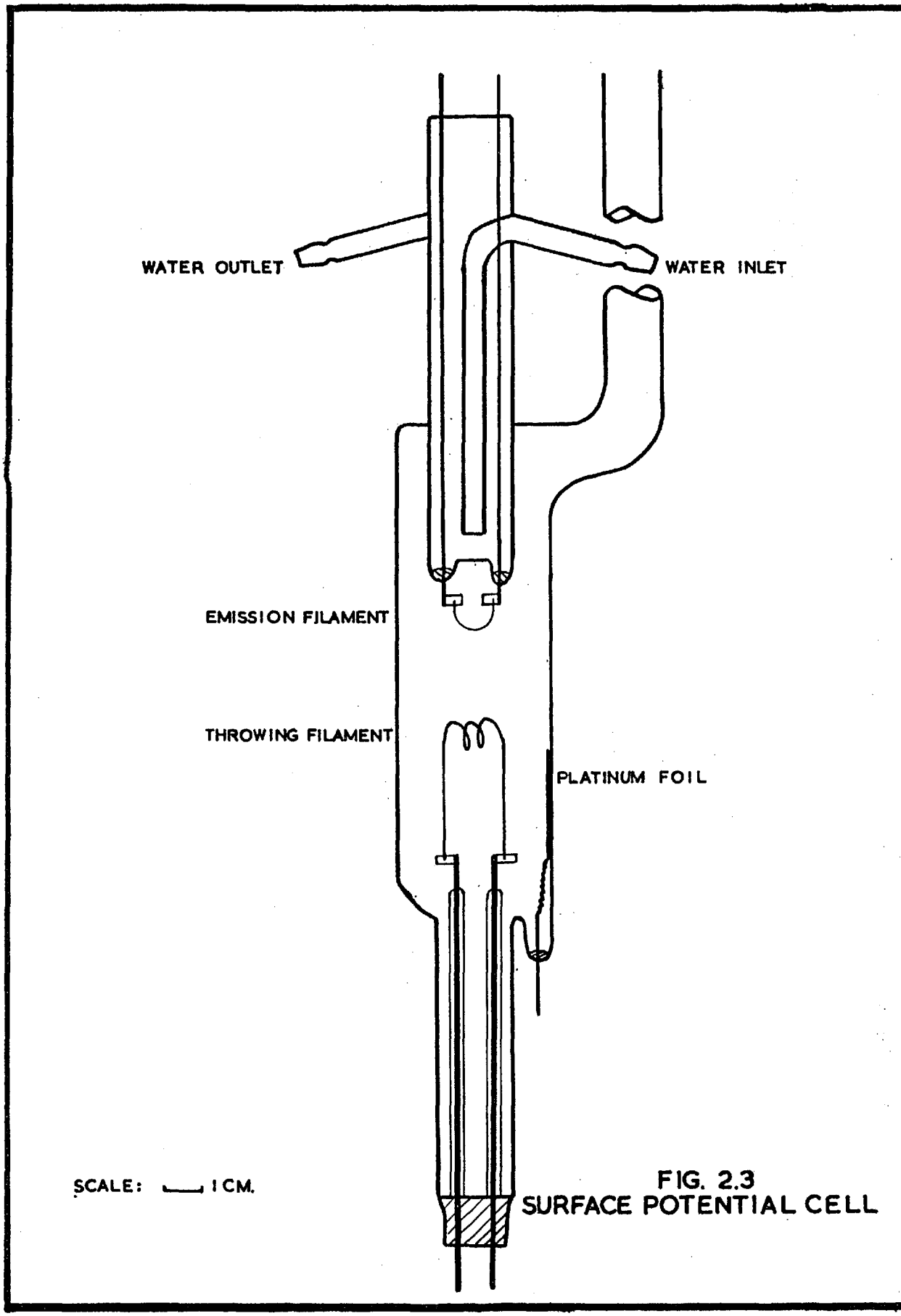


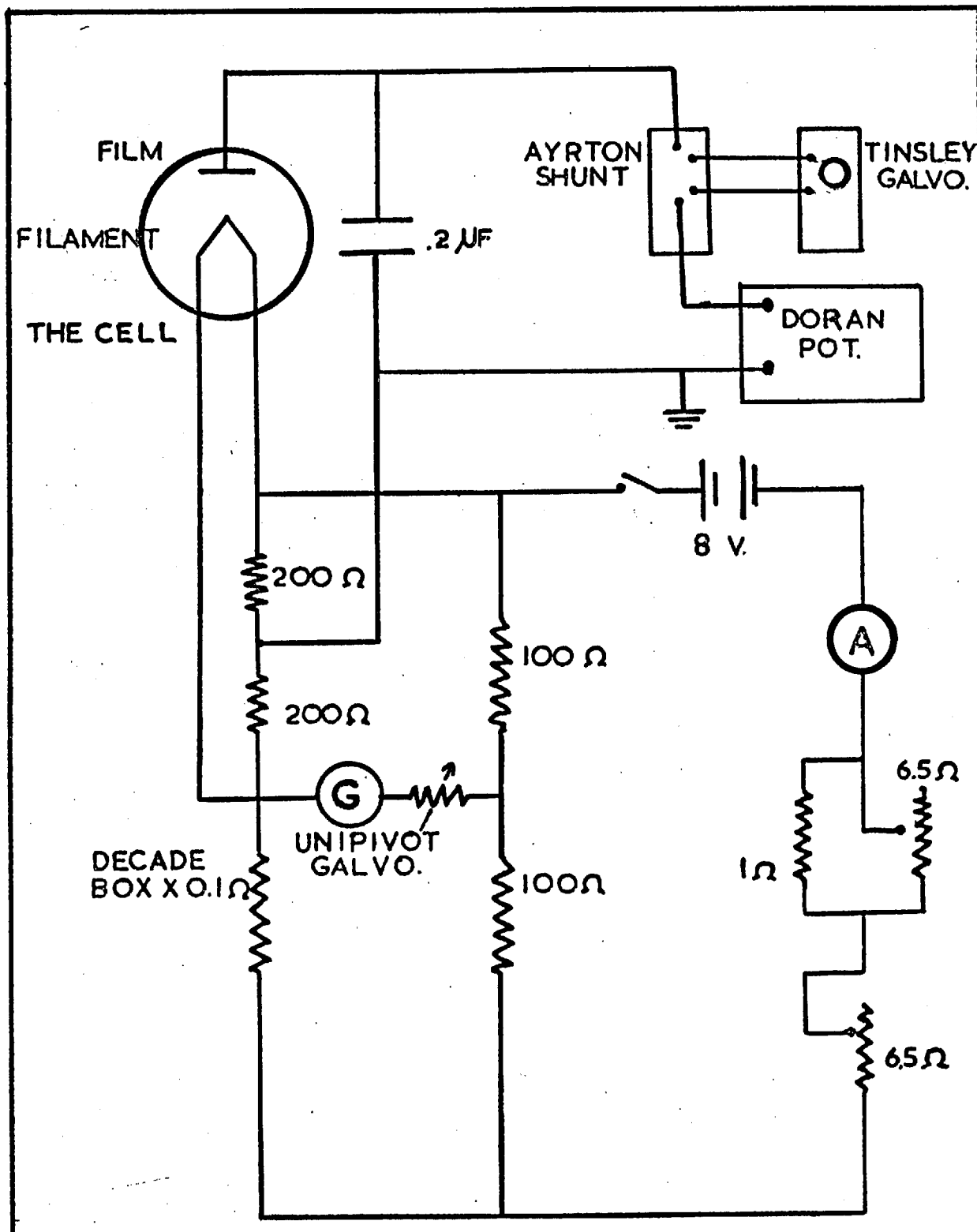
FIG. 2.3
SURFACE POTENTIAL CELL

a 1 cm length of 0.0025" diameter tungsten wire spot welded through nickel strip to a pair of 1 mm tungsten rods. To maintain the cathode at a temperature which was constant regardless of the environment of the cell, water was passed around these leads. In this way the temperature and hence the emission did not vary when different temperature baths were placed around the cell, otherwise it would not have been possible to differentiate between current changes resulting from S.P. alterations and those from emission current changes. With baths below 0°C the water flow was carefully maintained always otherwise resulting freezing would have destroyed the cell.

The throwing filament was a spiral of the metal wire mounted via a nickel strip to 2 mm tungsten rods. The evaporation current was supplied by a heavy duty step-down transformer feed by a Variac transformer. In this way it was possible to have a fine control on the current through the filament. An ammeter in series with the filament measured the throwing current.

2.2.5. Surface potential measuring circuit

In using the space charge limited diode method one is essentially measuring the "characteristic", or current/voltage (i/v), slope of a diode. Two methods are therefore possible; in the first the resistance of the diode is determined, e.g. by a bridge balance, for various applied voltages. This method is used by Mignolet(139) The second method is to measure the current passing through the cell at varying applied voltages; this procedure was used in the present work.



DIODE CIRCUIT FIG 2.4

The circuit used to measure the i/v characteristic is shown in fig.2.4.

The cathode was a tungsten wire of diameter 0.0025" (0.063 mm) heated electrically to 2400 - 2500°K. The emission was governed by Richardson's equation

$$j = AT^2 \exp\left[-\phi/KT\right]$$

and it was therefore essential that the filament was maintained at a constant temperature throughout any given experiment, otherwise changes would have been equivocal, since they could have resulted from either emission or work function changes. The filament temperature was kept constant by maintaining it at a constant resistance.

To this end the emission filament was made one arm of a Wheatstone Bridge, and the balance obtained at the beginning of an experiment was maintained throughout.

The bridge was supplied by four 2 V lead-acid accumulators kept in a charged state for optimum constant voltage. Out-of-balance currents were detected by a Unipivot bench galvanometer in series with a variable shunt resistor. The current flowing through the bridge was controlled by fine and coarse rheostates. A current of approximately 0.7 amp was drawn from the cells.

A pair of 200 ohm resistors in parallel with the emitter was centre-tapped effectively to earth the filament at the centre position.

The current passing through the cell was measured by a Tinsley mirror galvanometer (Type H) of sensitivity 10^{-9} amp mm^{-1}. The galvanometer was shunted by variable Ayrton shunt, and damped by a 30 k.ohm resistor in series. To decrease a.c. "pick-up", the lead from the anode to the measuring circuit was screened and the electrical apparatus contained in an earthed shell. This was found to be preferable to the "floating" arrangement used by Pritchard[140] A 2μF capacitor between earth and the anode filtered out a.c. noise pick-up. The potential difference between the anode and cathode was controlled by a Doran potentiometer having a range of $\pm$ 1.8 volts.

2.2.6. Temperature baths

Sub-zero temperatures were obtained using organic liquids cooled to their melting point by liquid nitrogen. In table 2.1 a list of convenient refrigerant baths is given.

Table 2.1

Temperature Baths

Bath	Temperature ^{o}K
boiling nitrogen	77.3
boiling oxygen	90.0
melting isopentane	113.5
melting n-pentane	141.7
melting methyl cyclohexane	146.6
melting ether	160.0
melting toluene	177.0
slurry of solid CO_2 and alcohol	195.0
melting chloroform	210.0
melting diethyl malonate	223.2
melting chlorobenzene	227.0
melting methyl benzoate	260.6
melting ice	273.2

A thermostated bath was used to give temperatures above room temperature. The sensing element was an Electromethods thermometer with a range 0 - 100^{o}C used in conjunction with an Electromethods control unit. The heater was varied with the temperature required; at low temperatures a 25 watt immersion heater sufficed while higher temperatures required a 50 watt heater. Rapid changes of temperature were effected by a 300 W

immersion heater. The bath medium was Esso Bayol oil stirred electrically. This oil had two advantages over water; its vapour did not disturb the electrical measurements and having a low specific heat it permitted temperature changes to be made rapidly.

The thermostat bath was readily converted to a cryoscopic bath for temperatures between $0^{\circ}C$ and room temperature. Whereas in the thermostat arrangement the relay switched on the heater if the bath temperature dropped below that desired, in the cryoscopic bath the relay operated a small centrifugal pump if the desired temperature was exceeded. The pump circulated ice water through a copper coil ($^{1}/_{4}$" bore, length 12") immersed in the oil. This arrangement maintained a given temperature to within $\pm$ $0.1^{\circ}C$.

2.3. Procedure

2.3.1. Preparation of cell

Evaporated films from previous experiments were dissolved by acids. However, tungsten was persistent in its adhesion to glass. It was found most convenient to rinse the cell initially with a strong solution of sodium hydroxide and to follow this with a warm solution of 2 - 5% hydrofluoric acid. The acid did not appear to dissolve the tungsten but merely lifted it from the glass substrate. The initial use of sodium hydroxide solution had no visible effect but omission of this step necessitated the use of a stronger solution of hydrofluoric acid

and this resulted in irksome etching of the cell interior. The cell was then washed repeatedly with distilled water.

The filament to be evaporated was prepared by winding aa spiral of the wire, generally three turns of diameter about 5 mm. Copper, having a low melting point, was thrown from a filament of tungsten wire around which was wound the copper wire. Details of filaments used are given in table 2.2.

Table 2.2

Filaments

Metal	Diameter	Current (A) to	
		Outgas	Throw
tungsten	0.25 mm	7.2	9.2
iron	0.5 mm	3.4 (transition 2.2)	~4.4
nickel	0.5 mm	4.6	6.4
copper	16 s.w.g on.2W	3.1	4.5
	16 s.w.g on.3W	5.0	6.5
molybdenum	0.3 mm	5.0	6.8

2.3.2. Outgassing procedure

With the cell attached, the apparatus was pumped out, generally overnight. During this time the traps and Pirani were heated to ca 250°C by heating tapes and the cell to ca 350°C by a furnace. The dosing system was vigorously flamed to outgas it. After this procedure an accumulation rate of less

than 10^{-6} torr per hour was obtained. With a liquid oxygen bath around trap 1 and cut offs A and E raised (to prevent contamination from tap 1) the filament was outgassed. Details of current used are given in table 2.2. The duration of outgassing was generally 6 - 8 hours. Iron filaments use outgassed by cycling through the α - γ transition temperature as suggested by Tompkins[162] Copper and nickel filaments required reduction before outgassing. This was effected by heating to bright red heat in an atmosphere of hydrogen at 1 torr pressure and the dosing system flamed next morning.

2.3.3. Preparation of the film

Prior to evaporation of the film mercury was raised in A, B and F and liquid oxygen placed around trap 1. The Pirani was immersed in a solid CO_2/alcohol slurry and the current supply switched on. This allowed the Pirani system to reach a steady state. The emission filament was flashed a few times at about 2800°C to outgas it. The cell was then immersed in liquid oxygen and the current through the filament was slowly increased until evaporation proceeded. The thickness of the copper, nickel and iron film was increased until the glowing filament became obscured. Tungsten films were thrown for about 1½ hours after which time the filament normally fused.

Films were sintered by raising the temperature of the cell to 100°C. The traps were then surrounded by solid CO_2/alcohol baths since the vapour pressure of ammonia at 195°K is still 40 torr.

2.3.4. Dosing and S.P. measurements

The two tungsten rods holding the evaporating filaments were connected to the anodes lead to prevent the filament having grid action. Failure to do this would have lead to i/v curves which were not parallel nor, indeed, stable. The cell was immersed in a bath at the required temperature, generally -78°C. By varying the decade box R and the rheostats (fig.2.4) the resistance of the emitter was rapidly adjusted to give a total deflection of about 40 cm for a voltage range -.8 V to 1.6 V. Throughout the experiment R was invariant and the bridge controlling the temperature of the emitter was balanced by the rheostats.

The i/v curve for the clean film was obtained by measuring the deflection of the mirror galvanometer at applied voltages between -0.8 and +1.6 V, increasing V by step of 0.2 V. Care was taken to ensure a stable curve was obtained. Gas doses were admitted as described in §2.2.2 and the i/v curve determined for each dose. When a time dependence was to be measured one value of V was maintained and i against t noted. When equilibrium was obtained an i/v characteristic was taken to check for parallel curves. The experimental limits of S.P. values obtained from i/v plots were $\pm$ 0.01 V.

Kinetic experiments are described later.

CHAPTER 3

SURFACE POTENTIAL RESULTS AND DISCUSSIONS

3.1. Experiments to check diode

Before proceeding to investigate the surface potentials of new systems it was considered advisable to measure the surface potentials of well characterized systems to ensure that the diode was being operated under correct conditions.

3.1.1. Copper-hydrogen

Although copper cannot chemisorb hydrogen molecules, hydrogen atoms are readily adsorbed. As the hot emission filament in the space charged limited diode dissociates hydrogen molecules this method will give a surface potential with the copper hydrogen system. Thus Bloyaert et al[172] obtained a zero S.P. with the vibrating condenser method while with the diode method they obtained a value of -0.27 V at 293°K. Similarly Culver et al[160] reported a value of -0.35 V at 90°K. Figure 3.1 shows the i/v plots with increasing hydrogen coverage (the last few doses are omitted for clarity) obtained in the present work. The maximum surface potential obtained was -0.32 V at 90°K which is in good agreement with the above values. A later experiment to check a new cell design gave -0.35 V.

3.1.2. Nickel-oxygen

At 289°K the nickel/oxygen system gave a maximum surface potential of -0.48 V which increased to -0.75 V at 90°K on the

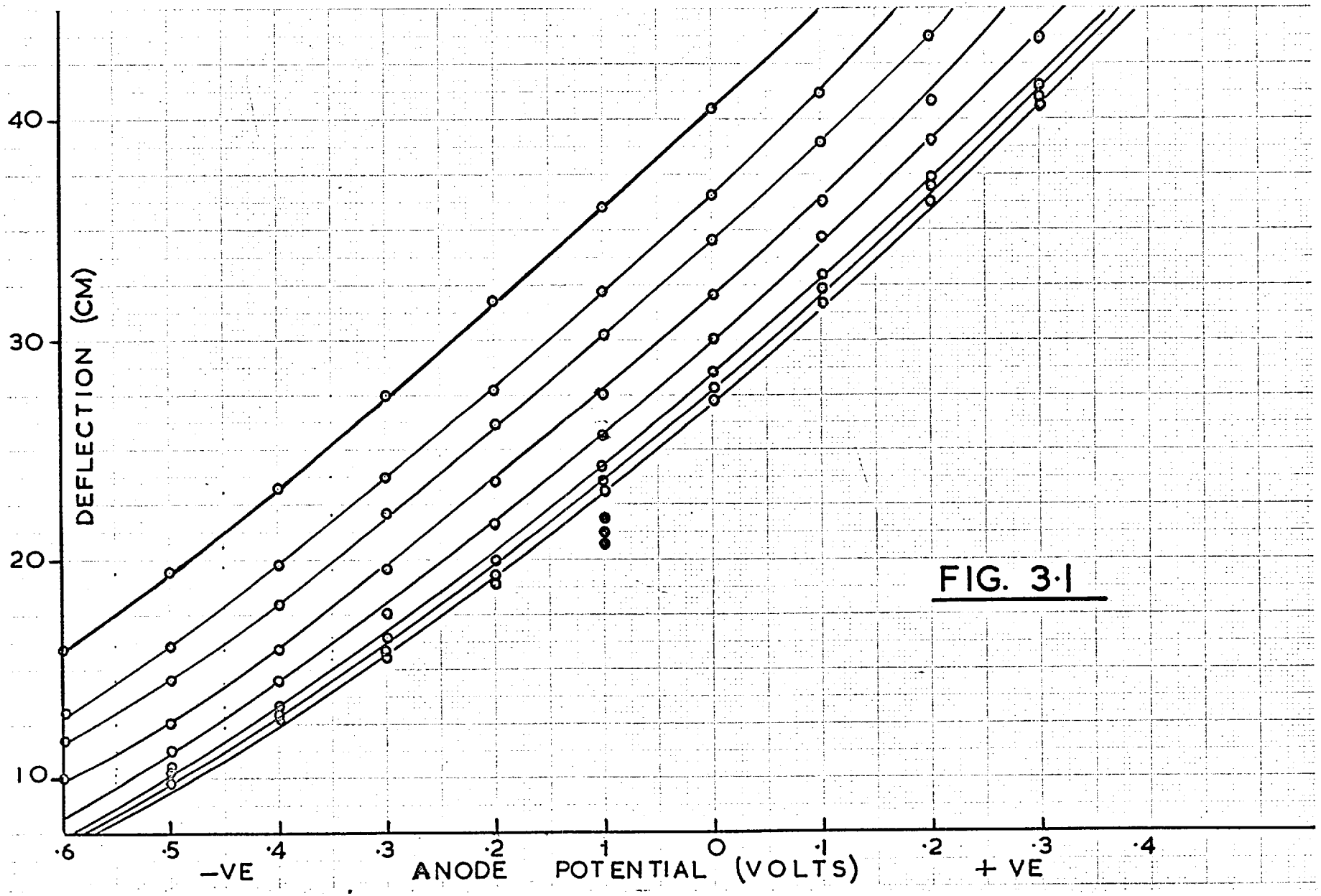

40
30
20
10
DEFLECTION (CM)
·6
·5
·4
·3
·2
1
0
·1
·2
·3
·4
–VE
ANODE POTENTIAL (VOLTS)
+ VE

FIG. 3·1

addition of more oxygen. This is in fair agreement with the value of -0.55 V (at 290°K) of Ogawa et al[189] but not with Mignolet[126] or Siddiqui[179] who obtained -1.6 V at 83°K and -1.3 V at 90°K respectively. However Delchar[133] measured the S.P. as 1.60 V at 90°K which, on raising the temperature, became increasingly less negative finally reaching -0.43 V at 273°K. The pressure dependence of the surface potential observed by Delchar was not investigated as it was not advisable to subject the hot tungsten emitter to oxygen in the gas phase. The complex S.P./pressure relationship led to the abandonment of this system as a check on the diode.

3.1.3. Tungsten-hydrogen

Initial experiments with tungsten were disappointing as very thin films were obtained at the stage when the filament fused. By maintaining a lower throwing current (9.1 A) and consequently a longer time, about 1½ hours, thicker films were obtained. The value of -0.55 V obtained was in good agreement with the literature values given in table 1.4. The i/v characteristics with increasing coverage are shown in fig.3.2.

3.2. The tungsten-nitrogen system

As this work is concerned with the reaction of ammonia and its constituents on a tungsten film an investigation of the W/N_2 system was undertaken. This was necessitated by the lack of agreement (§1.6.5) as to the S.P. of this system. While it was

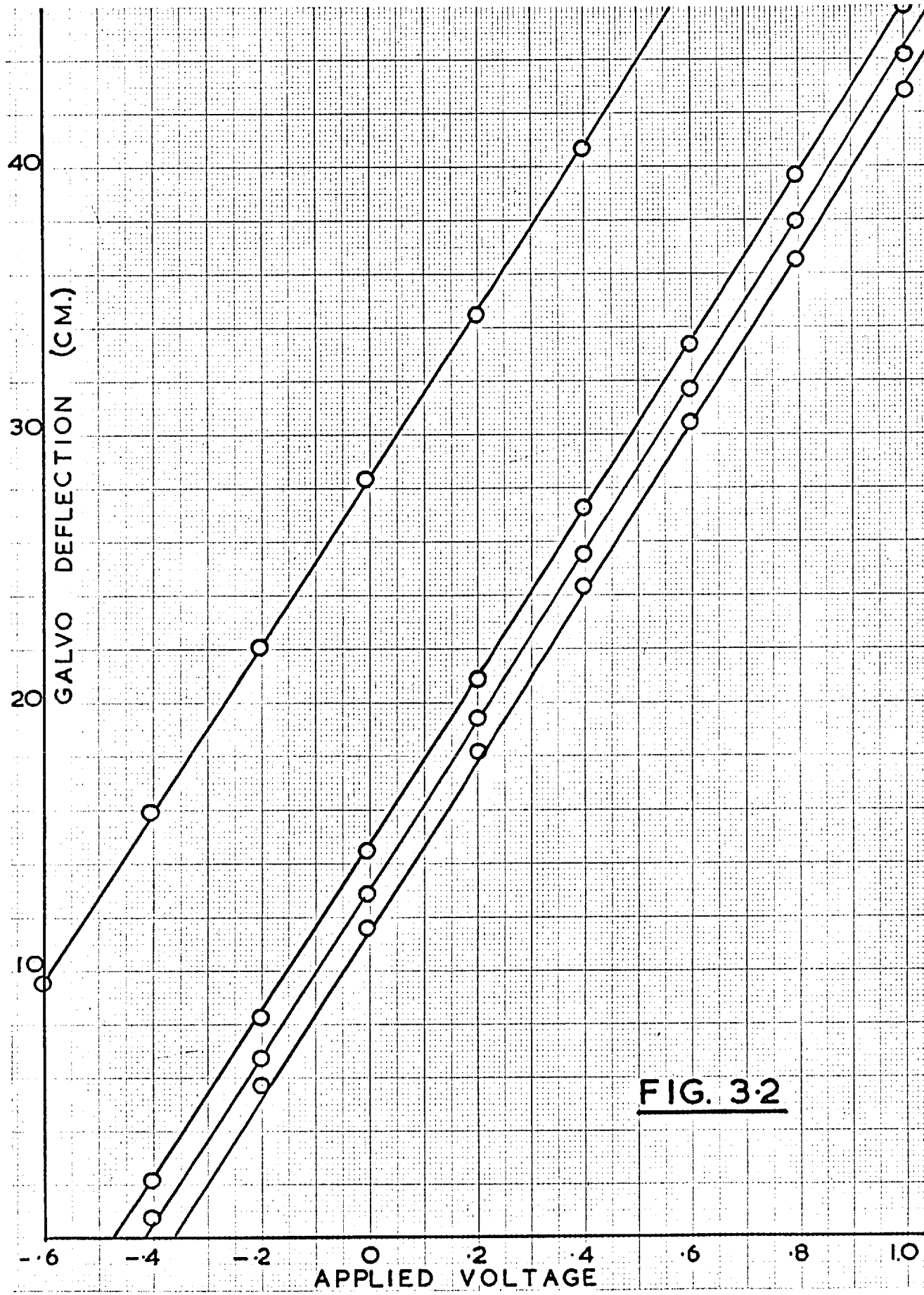


FIG. 3·2

not considered that the present work would resolve this disparity it was essential to observe the value obtained in the apparatus used in order to interpret later results.

3.2.1. The experiments on N_2/W

In the initial experiments(≠18)with W/N_2 a maximum surface potential of -0.27 V at 90°K was obtained. The pressure at this point was still $<10^{-6}$ torr. After pumping for 3/4 hr the S.P. became more negative reaching a value of -0.34 V. However, a number of experiments consistently gave lower values which increased on further addition of nitrogen at 293°K (see table 3.1). The results of ≠18 appear to be due to contamination

Table 3.1

S.P. of N_2 on W.

T°K	Experiment ≠							
	21	23	24	25	26	28	29	36
90	-0.18	-0.16	-0.18	-0.20	-0.17	-0.16	-0.20	-0.17
293		-0.38	-0.40	-0.45		-0.45		-0.45

In a further series of experiments the temperature dependence of the surface potential was closely examined. Thus in ≠81 the following thermol cycle was followed :

(1) a film with a nitrogen coverage of 2.2×10^{17} molecules at 77°K exhibiting a S.P. of -0.13 V was warmed to 90°K and the S.P. became -0.17 V.

(2) the film was warmed to 195°K whereupon the S.P. increased to -0.47 V,

(3) the film was warmed to 273°K, the S.P. decreased slightly to -0.45 V,

(4) the film was warmed to 293°K without causing a S.P. change,

(5) the film was warmed to 318°K again without change in S.P.,

(6) the film was cooled to 90°K, the S.P. remained at -0.45 V until 1.6×10^{17} molecules of N_2 were added which returned the S.P. to -0.13 V. A further addition of nitrogen (1×10^{18} molecule) did not change the S.P.,

(7) the film was warmed to 293°K and the surface potential increased to the more negative value of -0.45 V.

The surface potential changes throughout the cycle are shown in fig.3.3. On warming from T_1 to T_2 the S.P. alteration took less than 2 minutes before reaching a value at which it was stable for at least the 15 minutes of observation and, furthermore, did not change on addition of 5.4×10^{16} molecules of nitrogen. Cooling from T_2 to T_1 did not change the S.P. until gas was added. In fig.3.4 the effect of gas addition is illustrated. When, in step 7, the S.P. had reached -0.13 following the addition of 5 doses of N_2 a further amount of nitrogen (20 doses) did not alter the S.P.

Experiment ≠84 mirrored the results of ≠81. The surface potential changes with temperature are shown in fig.3.5. The temperature was raised in steps between 77°K and 360°K.

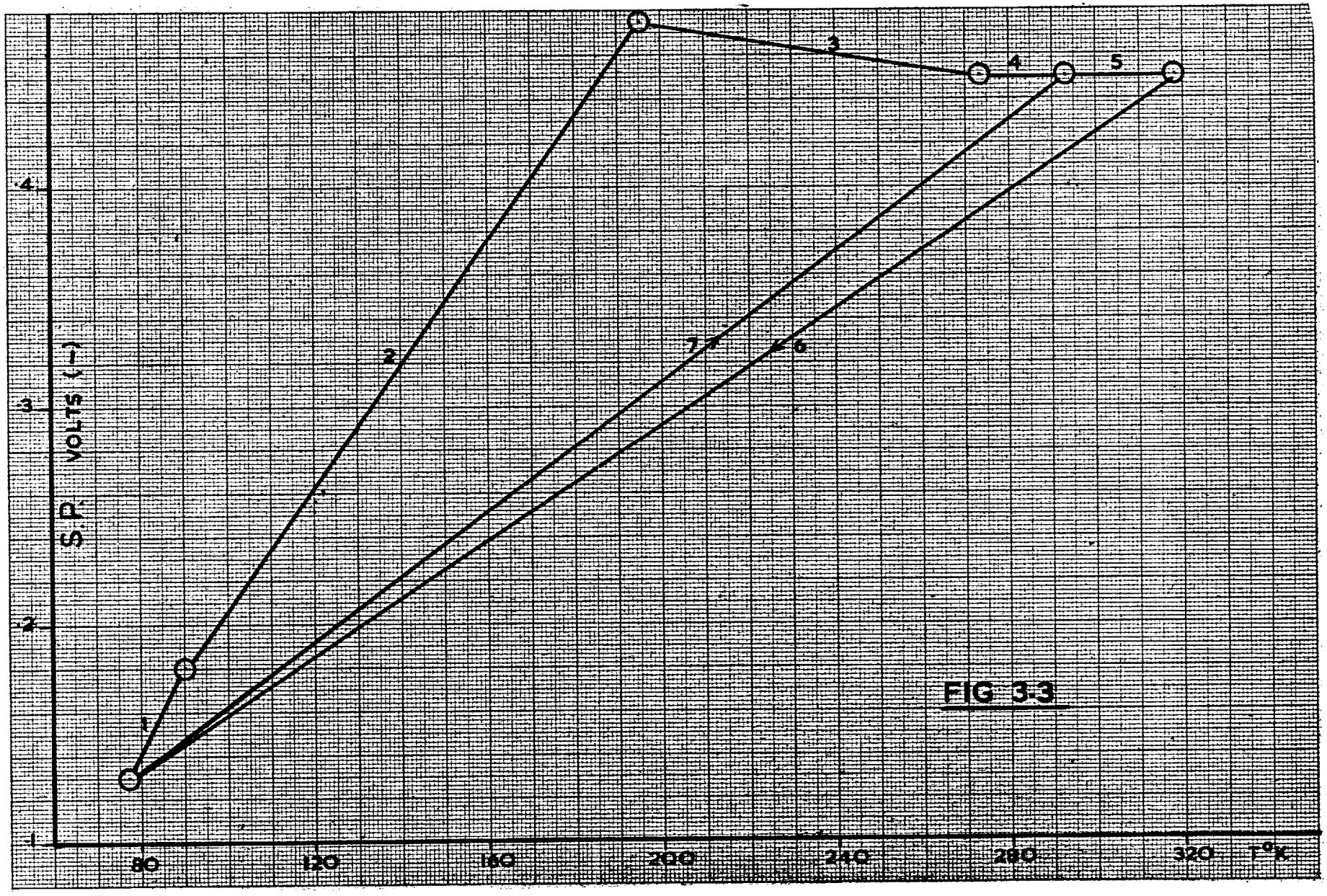


FIG 3-3

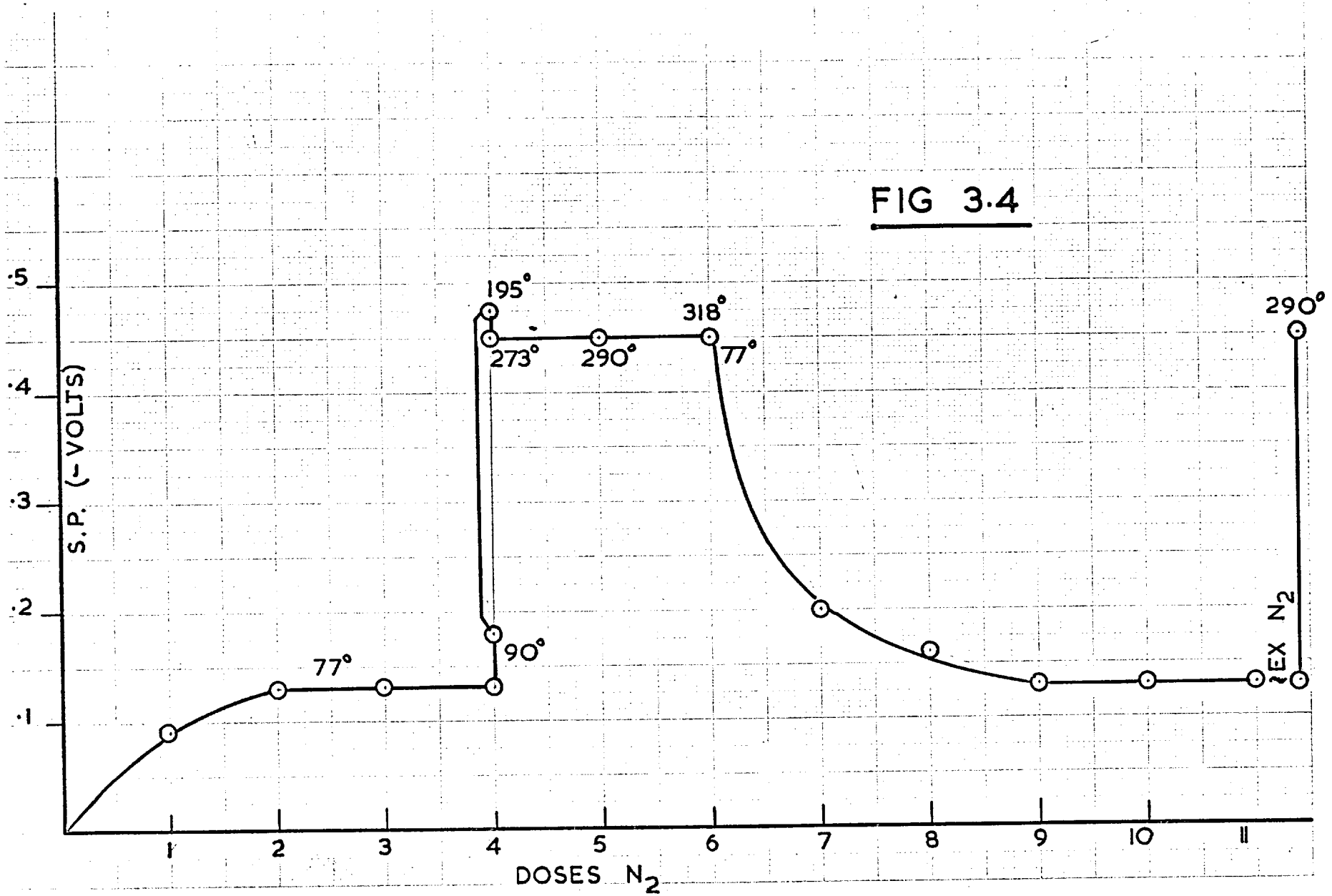


FIG 3.4
S.P. (- VOLTS)
·5
·4
·3
·2
·1
195°
318°
290°
273°
290°
77°
77°
90°
≈EX N2
1
2
3
4
5
6
7
8
9
10
11
DOSES N2

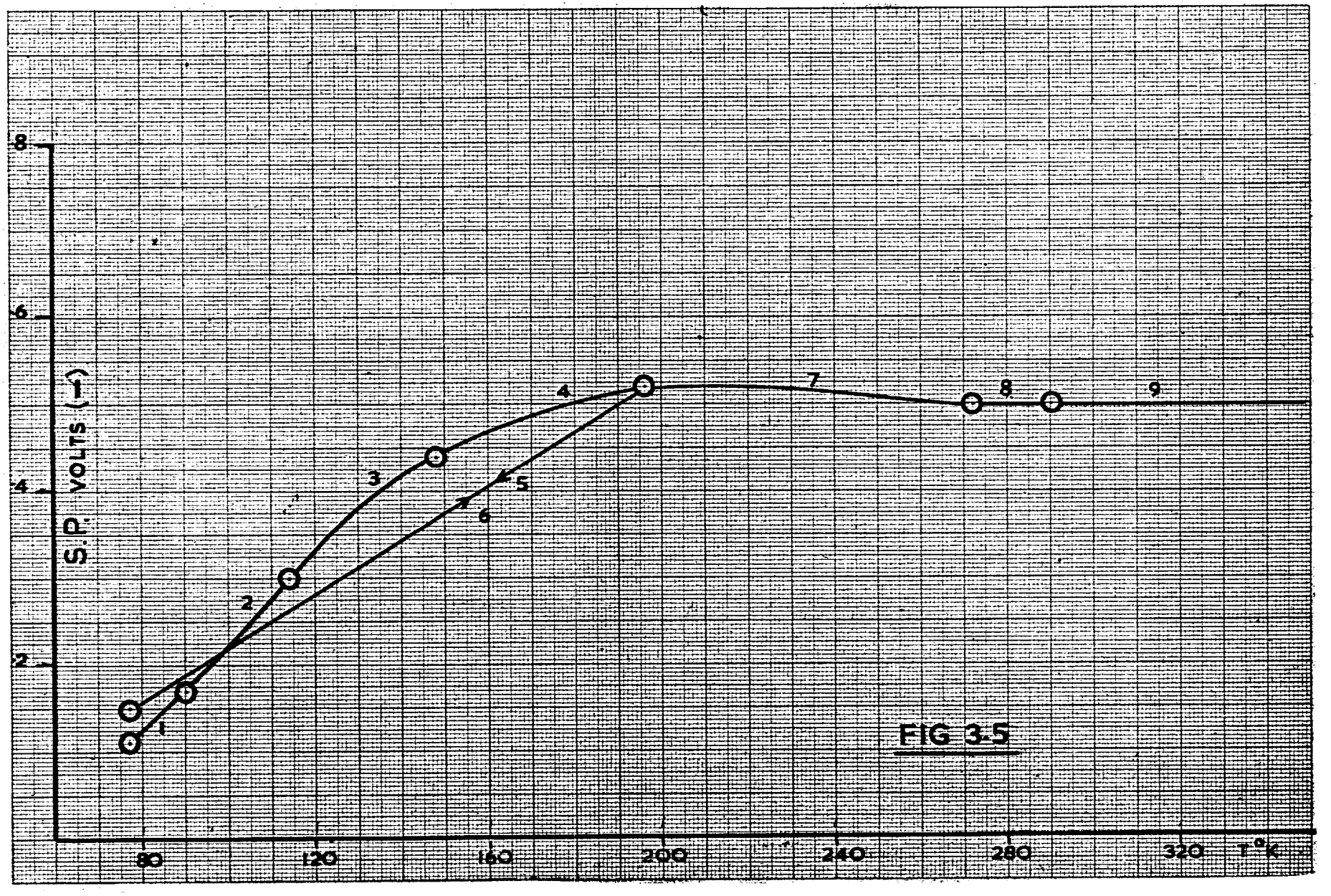


FIG 3.5

The maximum S.P. of -0.55 was obtained at 195°K, above which temperature there was a slight drop in the S.P. Again raising the temperature caused a spontaneous change in the S.P. to an increasingly negative value. Lowering the temperature had no effect until gas was added whereupon the surface potential returned to its original value.

These results may be summarized diagrammatically by fig.3.6.

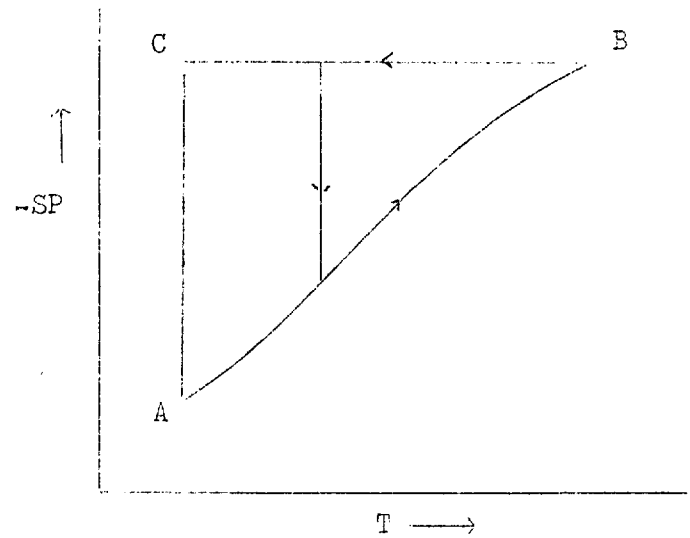


Fig.3.6

A temperature increase caused the surface potential to follow the curve AB; a temperature decrease had no effect upon the S.P. (line BC) until nitrogen was added whereupon the surface potential recovered its original value at that temperature (projection of BC on AB).

The near constancy of the surface potential after 195°K was again observed. At 290°K the S.P. was observed to remain steady for two hours. Raising the temperature to 366°K had no effect upon the

surface potential nor did addition of N_2 at that temperature.

In a number of experiments it was noticed that when the surface potential at 90°K had reached its maximum value of -0.18 V subsequent doses of nitrogen gave an initial surface potential of -0.16 V but this rapidly increased to -0.18 V. This "positive transient" will be discussed later.

In one experiment, ≠86, the film was first dosed with nitrogen to give its maximum surface potential of -0.14 V at 77°K and was then saturated with nitrogen (2.54×10^{18} molecules were adsorbed) and the cell pumped out. On warming to room temperature (292°K) there was a momentary pressure rise (ca 2×10^{-5} torr) which rapidly decreased to less than 10^{-6} torr. The S.P. was the -0.54 V when in another experiment the dosing pattern was repeated but the temperature raised by small intervals a curve nearly identical to that of ≠84 was obtained. Gas pulses were not observed, perhaps because they were too small.

In ≠88 the addition of 2×10^{17} molecules of nitrogen to a film at 293°K produced a S.P. of -0.32 V. Cooling to 77°K was again without effect on the surface potential but the addition of 2.5×10^{17} molecules of N_2 at this temperature increased the S.P. +0.1V. Warming to room temperature gave a spontaneous change back to -0.33 V. Nitrogen addition at 77°K once more returned the surface potential to +0.1 V. The vacillation between +0.1 V at 77°K and -0.33 V at 293°K (or 195°K) was repeated twice more. The same sequence was found in experiment ≠89 and ≠91. It thus

appears that, while the reversible surface potential/temperature relationship is maintained, the temperature of initial dosing makes the surface potential ca 0.23 V more positive.

3.2.2. Discussion

A review of the various reports concerning the surface potential of nitrogen on tungsten has been given in § 1.6.5. The value of -0.55 V at 290°K obtained in the present work agreed with the originally accepted value. The positive S.P. of 0.10 V observed by Ehrlich when nitrogen was gettered by a nickel film was not observed in a series of experiments using nitrogen so gettered. From the specification of the nitrogen (§ 2.1.1) and considering the quantity of gas used (ca 1 x 10^{18} molecule) to develop the surface potential in these experiments it would have been surprising if the removal of the small impurity contact by gettering had, indeed, significantly altered the recorded value. The measured surface potential is an average of all work function alteration over the entire surface hence impurities in small concentrations have little effect when working with a large surface area. This is one of the advantages of using evaporated metal films. The surface contamination can be made comparable to that of flashed filaments by outgassing the metal and throwing the film under good vacuum conditions. The surface area of a film is many order of magnitude greater than that of a wire or ribbon, as a film has a larger geometric area and a great "roughness factor". In the case of field emission

microscopy the number of sites available for adsorption is very small, hence the nitrogen must compete against the more strongly held impurities. Furthermore, the most likely impurities, CO, CO_2 and O_2, have, per capita, a greater effect upon the work function of the metal. It does, indeed, seem likely that the diversity of results reflects the difference in the method of evaluation[138]. Ehrlich[47] has shown a marked surface specificity in the case of α and γ states. The surface potential will therefore also be dependent upon the crystallographic face most dominant in the metal adsorbent.

The observed surface potentials outlined in the section above are, in part, in accord with the results of Delchar[133]. At 77°K he obtained a surface potential between 0.15 and 0.20 V which reached a maximum of -0.50 V at ca 190°K. As the temperature was increased the surface potential became less negative reaching ca -0.4 at 290°K. In one experiment it actually became slightly positive (+0.09 V) but in this experiment the maximum value, at 190°K, was only -0.36 V. The decrease after 195°K was much less (0.05 V) in the present work. There was further agreement in that the addition of gas at 290°K following this warming up left the surface potential unaltered. But addition of N_2 at 77°K returned the surface potential to -0.10 V. The appearance of a gas pulse from a saturated film on warming to 290°K was also reported as was the positive transient. The fact that two very dissimilar

methods of measuring surface potential, viz the static condenser and the space change limited diode, when used in conjunction with evaporated metal films gave results so much in agreement is surely evidence for the above contention that the surface potential is a function of the physical nature of the adsorbent. Hill and Pethica[138] have suggested that their positive value of 0.1 V as opposed to their original -0.50 V may have been obtained because the alteration in the flashing technique changed the surface structure.

The complexity of binding states discussed in 1.3.2 may be used to explain the present results. It has been shown[181] from flash filament studies that the γ state is completely desorbed at 190°K. Thus as the film was warmed from 77°K to 198°K the γ population decreased to zero. As this species is considered to be molecular nitrogen, weakly held with a binding energy of ca 9 kcal/mole., it will therefore have a positive dipole outwards, thus removal of the γ species causes the S.P. to become more negative. The process of desorption of the β state will have a high activation energy. Therefore cooling to 77°K will not restore the γ/β equilibrium to its original value. But addition of nitrogen at the low temperature will replace the γ state and give a less negative surface potential.

It is more difficult to explain the difference between

(a) the surface potential of -0.55 V obtained by initially dosing at 77°K (S.P. = -0.14 V) followed by warming to 290°K (ca 195°K) and

(b) the development of a surface potential of -0.32 V when the initial dosing was at 290°K.

Ehrlich has shown that the population of the α state was decreased as the temperature of initial dosing was raised. To use this to explain the above difference would require the α state to have a negative dipole outwards. However, this state is held molecularly and a positive dipole outwards would be a more reasonable assumption. Indeed Delchar has used such a positive dipole to explain the decreasingly negative surface potential at temperatures above 190°K. The explanation may be connected with Ehrlich's observation that nitrogen adsorbed at room temperature is immobile. Perhaps this alters the distribution of the various species.

The small positive transient formed when nitrogen was admitted to a film which has already adsorbed sufficient nitrogen to develop its maximum surface potential may be explained. As the dose of N_2 enters the cell it is initially held molecularly on top of the chemisorbed nitrogen and it rapidly migrates over the surface to find a vacant site for chemisorption. The physically adsorbed N_2 will, while it remains, make the surface potential less negative. As it is adsorbed on a film already exhibiting a maximum surface potential it will enter the "inner surface" of the film and not change the surface potential when it is chemisorbed.

3.3. The surface potential of ammonia on tungsten

3.3.1. Surface potential at 195°K

In a large number of experiments to measure the surface potential of ammonia on tungsten values between +1.7 V and +2.0 V were obtained with a heavier weighting on the higher values, The surface potential is therefore taken as +1.9 ± 0.1 V at 195°K.

When the film had been thrown and annealed, the i/v characteristic was plotted. At this stage, with the emission filament on, small doses of about 5 x 10^{16} moles of ammonia were added. As reported by Gundry et al[141] the initial doses of ammonia were without effect on the surface potential. In a series of experiments (≠40 - 48) this effect was examined. Doses of ammonia were added to the adsorption system without a film. The first four doses were adsorbed by the glass surface of the U-tubes and Pirani, and the pressure remained at less than 10^{-6} torr. The fifth dose gave an equilibrium pressure of ca 10^{-5} torr. This corresponds with the observation that, in general, the first two doses had no effect upon the surface potential. The ammonia which entered the apparatus had to pass through the traps to reach the film and only when the coverage on the glass was great enough to slow down the ammonia adsorption was the film able to compete for the ammonia. Thus the third dose was able to alter the surface potential.

To substantiate this hypothesis ammonia was admitted to the system for 10 minutes at a pressure of ca 10^{-1} torr, with the

traps and Pirani at 195°K and the cell at 373°K. In this way the glass surface of the traps and Pirani were saturated with ammonia. The apparatus was pumped out and the film thrown in the normal way. The first ammonia dose caused a shift in the i/v characteristic. Figure 3.7 shows the surface potential increase with dosing for a number of these experiments. Basically the difference between such experiments and others in which the glass saturation step was omitted was that the data (S.P. vs n) for the former passed through the origin of the graph while the latter did not do so (fig.3.8).

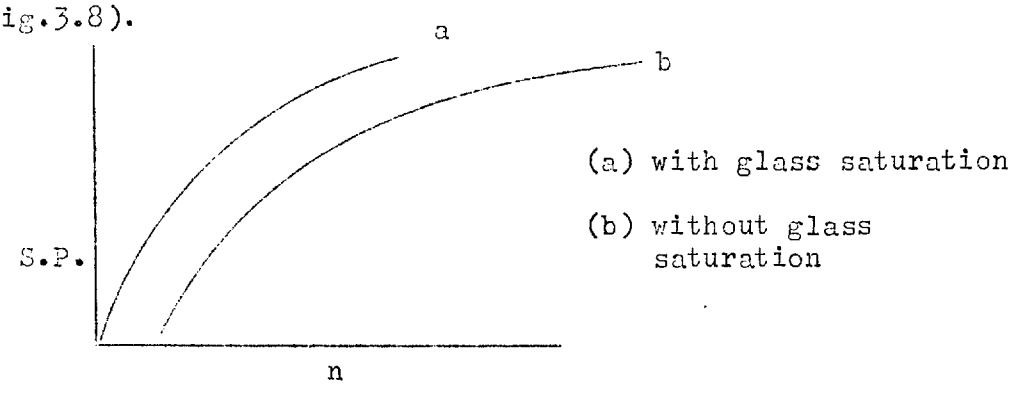


Fig.3.8

In experiments without pre-adsorption of ammonia on the glass surface it had been observed that upon addition of an ammonia dose (not one of the first few) the surface potential changed slowly. With pre-adsorption of ammonia the surface potential was still not instantaneous but somewhat more rapid. The galvonometer deflections against time are shown below for two such experiments.

Experiment ≠38 was performed without pre-adsorption and ≠42 with pre-adsorption.

≠38	t (mins)	0	2.5	4.0	10.5	15.0	18.0	23.0
	d (cm)	28.7	29.0	29.4	30.0	30.4	30.6	30.8
≠42	t (mins)	0	0.5	2.5	3.5	4.5		
	d (cm)	20.9	21.4	22.0	22.0	22.0		

These deflections were at zero applied voltage for the fifth and third dose respectively; these are comparable as the first two doses in ≠38 had no surface potential effect.

Later pressure/time measurements showed doses, some 100 fold greater than used in surface potential experiments, were adsorbed within a few minutes. Thus the time dependence of the surface potential appears to be due not to the slow ammonia uptake but to the slow diffusion of ammonia through the traps. However, a slow surface reaction is not excluded. Attempts were made to analyse the surface potential/time relationship into first or second order processes. Although the data gave fairly straight lines when fitted to the equation

$$k = 2.303 \frac{\Delta \log(\phi_\infty - \phi_t)}{\Delta t}$$

the velocity constant so obtained varied greatly in no apparent pattern from one dose to the next.

The average dose required to give the maximum surface potential was 5×10^{17} molecules whereas the film will adsorb a total of

of ca 4 x 10^{18} molecules. The surface potential measured when the doses were added with the emission filament on and that obtained by allowing each dose to be adsorbed and then switching on the filamer were identical. Surface potential measurements at high coverage were difficult especially when hydrogen was also adsorbed because the emission filament caused an evolution of hydrogen. This altered the system under investigation and, more seriously, as the pressure increased the diode ceased to operate under correct conditions. In an attempt to aleviate this problem an emission filament was coated with lanthenum hexaboride to give an emitter of lower work function and then one which would give a reasonable current at a lower temperature. The coating was very readily made by dipping the tungsten wire in a slurry of lanthenum hexaboride in methyl alcohol and applying a potential of 100 V between the wire and a Pt electrode. The filament was very rapidly coated by electrophoresis. Although the coated filament was extensively outgassed it gave a poor surface potential result; perhaps this was because the lower temperature allowed chemisorption on the filament. Furthermore, hydrogen was still evolved from a saturated film. It appears that this evolution was caused by electron bombardment rather than a thermal effect.

3.3.2. Effect of temperature

When the temperature of a tungsten film exhibiting the maximum surface potential at 195°K was increased the surface potential decreased. The results of a number of experiments are shown in

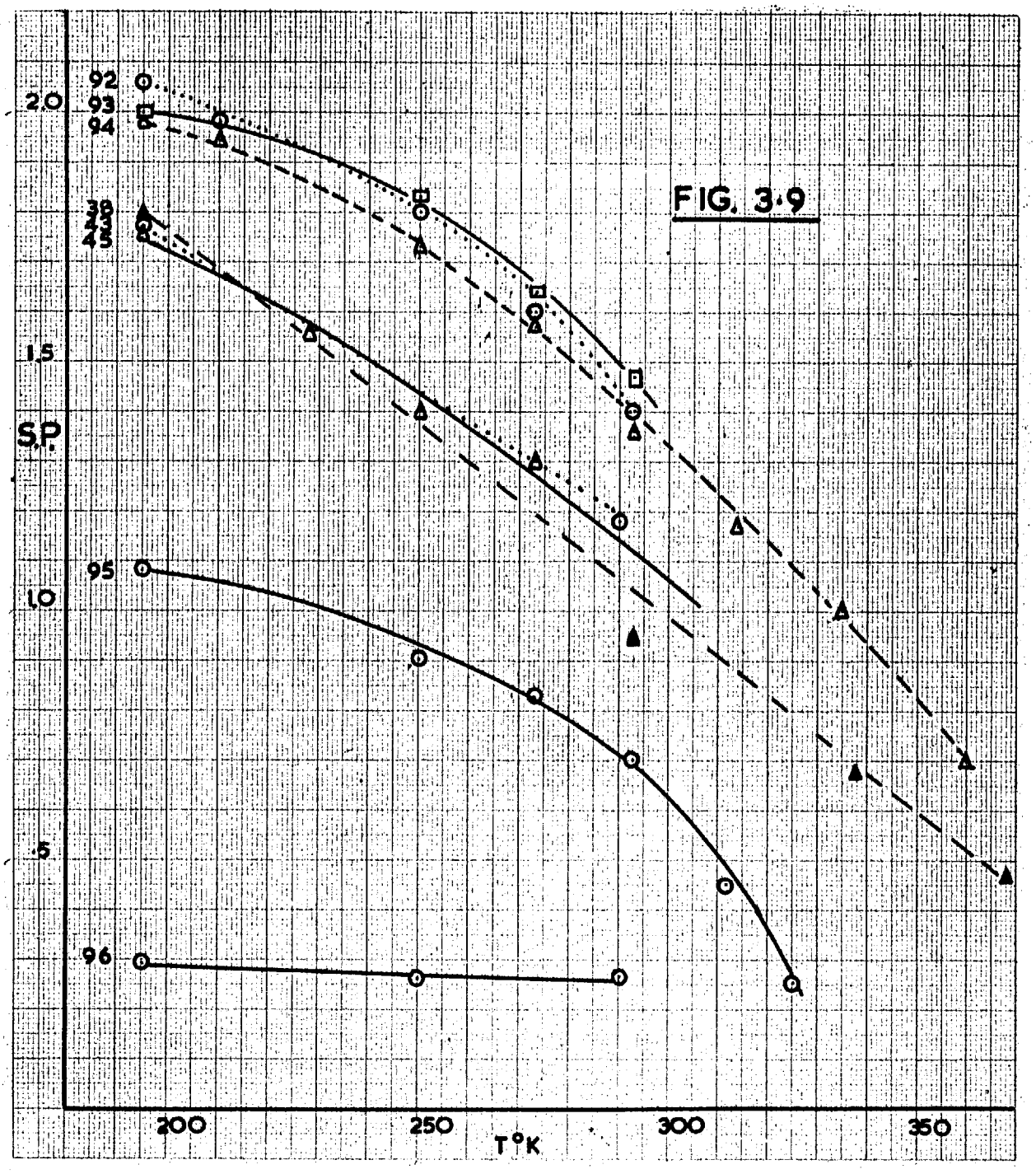
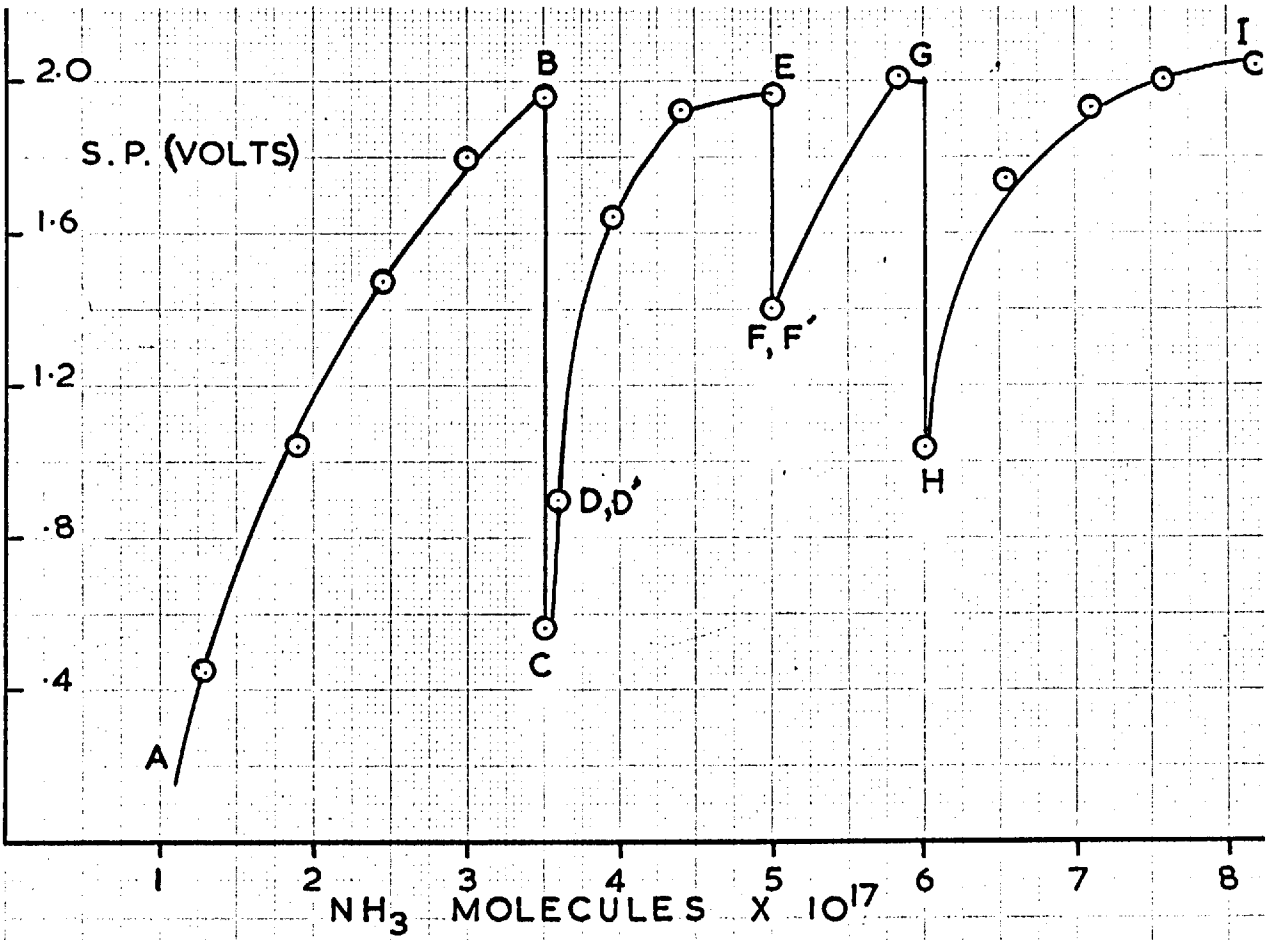


FIG. 3·9
92
93
94
38
43
45
95
96
2.0
1.5
1.0
.5
S.P.
200
250
300
350
T°K

fig.3.9. Although the films fall into two series (≠38, 43, 45 and ≠92, 93, 94) having slightly different maximum surface potentials the profiles of surface potential against temperature are fairly parallel. Also shown in fig.3.9 are the surface potential/temperature relationships for films which had been so dosed as to give a surface potential lower than the maximum. The extremely small change in surface potential in the case of a film having a very light ammonia loading is very striking. Another interesting feature is the fact that the film having a surface potential approximately half the maximum has a SP/T curve nearly parallel to that of film with the maximum surface potential.

While the surface potential change on raising the temperature was too rapid to measure, on lowering the temperature the surface potential increased very slowly. In ≠44 the film exhibited a surface potential of 1.8 V at 195°K and on warming to 290°K this fell to 1.05 V. The film was then allowed to stand at 195°K for 2 hours and the surface potential recovered to reach 1.4 V. Similarly in experiment ≠46 a 25% recovery was noted after 90 minutes. Addition of more ammonia at 195°K gave a surface potential of 1.8 V. Similarly if no recovery had been allowed, addition of ammonia at 195°K returned the surface potential to its original value (cf nitrogen experiments). Figure 3.10 shows the effect of heating and then dosing a film at the lower temperature to recover the original surface potential. When the original dosing of ammonia



AB Ammonia added at 195°K

BC Hydrogen added (~ 3×10^{18} molecules adsorbed)

CD Warmed to R.T., 1.5×10^{17} molecules H_2 evolved, pumpted

DD' Cooled to 195°K

D'E Ammonia added

EF Warmed to R.T., 3×10^{17} molecules H_2 evolved, pumped

FF' Cooled to 195°K

FG Ammonia added

GH Warmed to R.T., H_2 evolved, cooled to 195°K, H_2 readsorbed

HI Ammonia added

FIG. 3.10

took place at 290°K a surface potential of 1.1 V was obtained; addition of ammonia to the film at 195°K gave a surface potential of +1.8 V. When a film was heated above 290°K the recovery was again noted. This is shown for one such film in fig.3.11 the step in which are :

AB ammonia 5.25×10^{17} molecules added to give maximum surface potential of +2.0.

BC excess ammonia added, 4×10^{18} molecules adsorbed.

CD warmed to 293°K, 4.7×10^{17} molecules of hydrogen evolved.

DE warmed to 367°K, 7.8×10^{17} molecules of hydrogen evolved.

EF cooled to 293°K, recovering in 12 hours.

FG cooled to 195°K, recovering in 1 hour.

GH ammonia added ca 3×10^{17} molecules to give a surface potential of 1.95 V.

An interesting result was obtained (fig.3.12) when the data of ≠94 were plotted as log(S.P.) against 1/T°K. The sharp discontinuity is interesting.

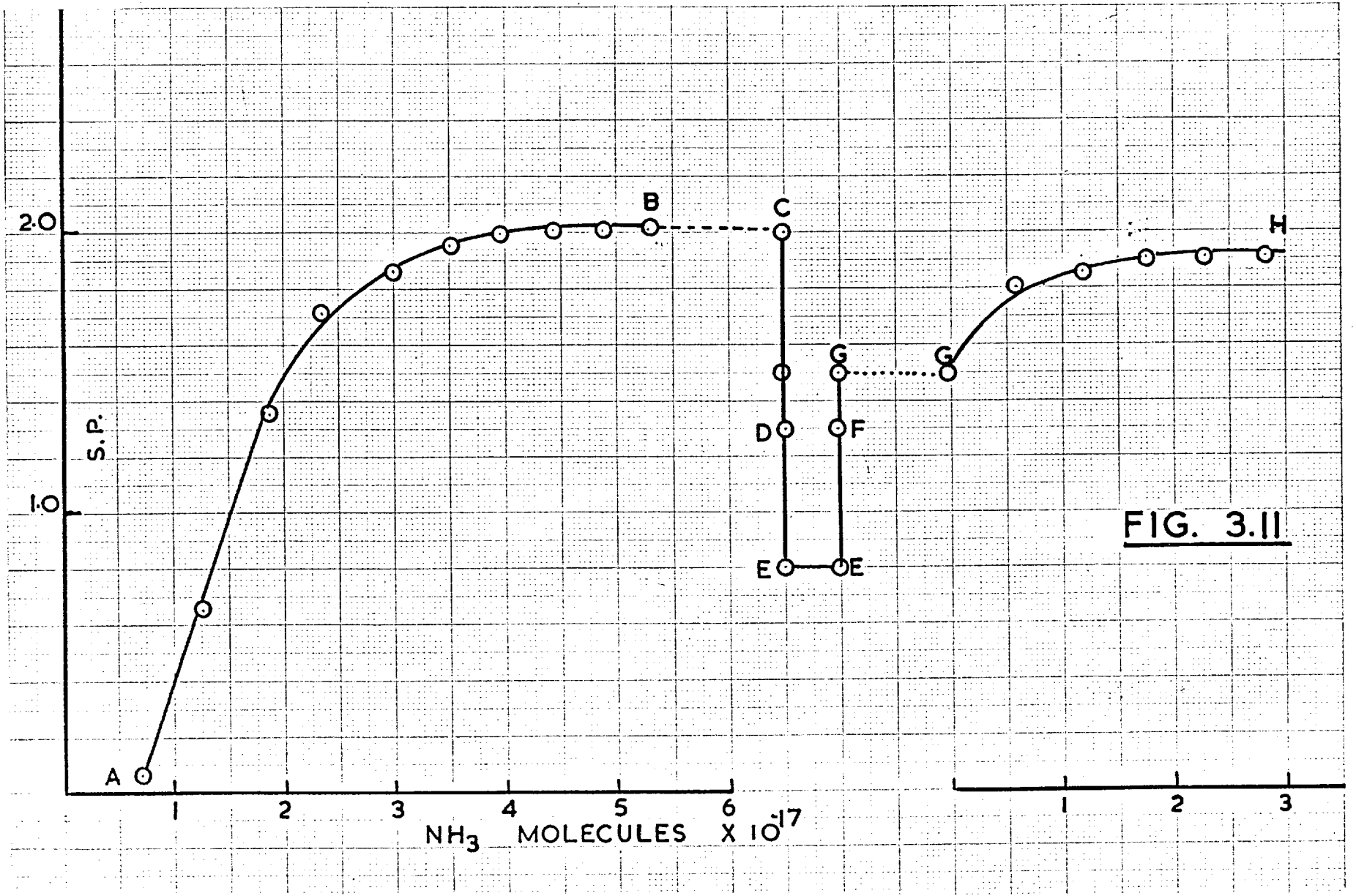


FIG. 3.11

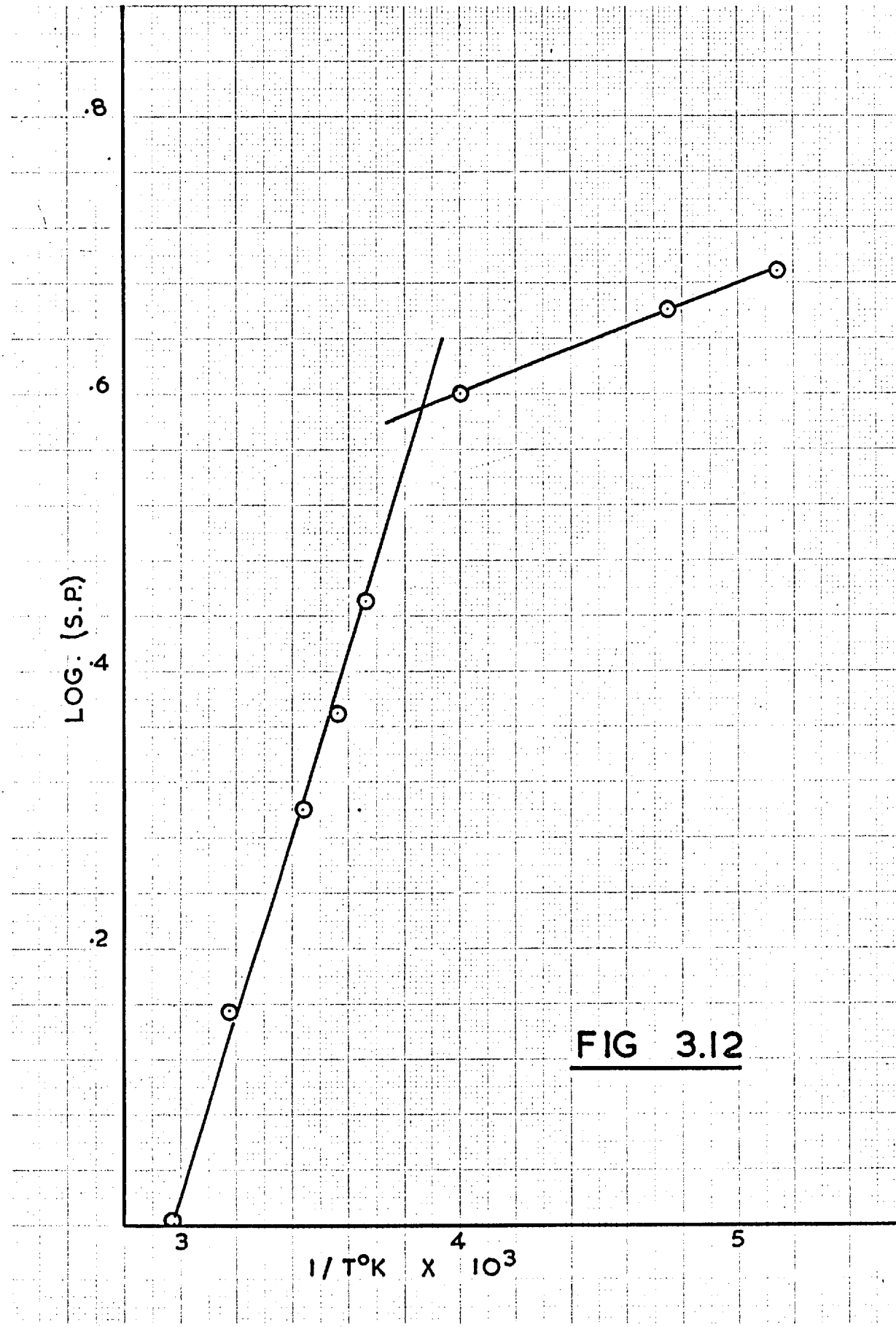


FIG 3.12

3.4. Surface Potential of ammonia, hydrogen and nitrogen

If ammonia is dissociatively adsorbed on tungsten

$$NH_3 \rightleftharpoons NH_2 + H$$

the addition of hydrogen would be expected to cause recombination in order to retain the equilibrium constant K. Similarly addition of nitrogen would be expected to enhance the ammonia dissociation by removing hydrogen atoms from the equilibrium system. The various species having different dipoles and/or polarizabilities would cause different surface potential effects. Experiments have been performed in an attempt to observe such effects. Hydrogen and nitrogen were added (a) before the ammonia, "pre-addition", (b) after the ammonia, "post addition" and (c) when insufficient ammonia had been added to develop its maximum surface potential, "inter-addition". The observed effects are of limited accuracy as the large surface potential of ammonia (+1.9 V) may have been great enough to cover up minor alterations caused by N_2 and H_2.

3.4.1. Pre-addition experiments of hydrogen

It has been established (≠49, 50, 61, 62, 66, 101 and 102) that the addition of sufficient hydrogen to give its maximum surface potential on a clean film had no sensible effect on the surface potential subsequently obtained by the addition of ammonia at 195°K. The amount of hydrogen required to develop its maximum surface potential was approximately the same as that required by ammonia on a clean film, viz. ca 5×10^{17} molecules. Furthermore the dose

of ammonia so required was unaltered by the presence of pre-adsorbed hydrogen. The surface potential/temperature profile of a H_2/NH_3 layer is identical to that obtained with an ammonia layer.

In experiment ≠62 the film was saturated with hydrogen at 195°K and ammonia added. While the addition did not cause hydrogen evolution, as soon as the emission filament was switched on, to measure the surface potential, hydrogen was evolved. If, however, the hydrogen adsorption to saturation took place at 290°K, and the film cooled to 195°K, surface potential measurements were possible when ammonia was added there being no hydrogen evolution. This gave a value of 1.8 V.

Although not a surface potential measurement, it is appropriate to record here that the presence of sufficient hydrogen to saturate a film at 198°K did not alter the amount of ammonia which the film would subsequently adsorb. The data are, of course, accurate only with the 25% variation in the surface area of the separate films thrown.

3.4.2. Post-addition of hydrogen

When hydrogen was added to a film exhibiting its maximum ammonia surface potential no effect was obtained until a comparatively large amount (ca 4×10^{18} molecules) had been added. In experiment ≠59 hydrogen was added until the film was nearly saturated, whereupon a small increment of hydrogen 5×10^{16} molecules caused the surface potential to decrease by 1.0 V and the next dose of 5×10^{16} molecules

was not all absorbed. The magnitude of the effect was dependent upon the hydrogen pressure. In ≠57 a film having an ammonia layer exhibiting a surface potential of 1.96 V was subjected to a hydrogen pressure of 10^{-4} torr, (about 3×10^{18} molecules of hydrogen were adsorbed).

Following the removal of the gas phase hydrogen the surface potential was +0.6 V. The film was warmed to room temperature and the evolved hydrogen pumped off. On recooling to 195°K and adding ammonia the surface potential rose to 1.93 V, i.e. substantially the same as before. In experiment ≠58 hydrogen was added to the film to give the maximum surface potential of -0.4 V and ammonia was added to give a surface potential of +1.95 V. The film was then cycled from 195°K to 290°K and back to 195°K. Then 2×10^{18} molecules were added and adsorbed without change of surface potential.

3.4.3. Inter-addition of hydrogen

Three experiments (≠71, 72 and 76) have been performed and gave interesting effects. Hydrogen was added to films having different ammonia loadings. The results are shown in fig.3.13. The initial dose (approximately 5×10^{16} molecules) caused a slight decrease in the surface potential and further addition of ca 3×10^{18} molecules increased the original surface potential by 0.2 V. Further doses were adsorbed but did not affect the surface potential. As in the pre-addition experiments, once a film had

been subjected to a saturating dose of hydrogen, it was necessary to warm the film and remove the evolved hydrogen otherwise the emission filament caused hydrogen evolution when surface potential measurements were attempted.

This warming process caused a decrease in surface potential but ammonia increased the surface potential to -1.8 V. In ≠76 fig.3.13c although the initial decrease caused by hydrogen was similar to that in ≠71 and 72, the second effect, the increase in surface potential, was larger than expected.

3.4.4. Pre-addition of nitrogen

The results of these experiments (≠51-52) were similar to those involving the pre-addition of hydrogen. That is to say there was no sensible effect on the surface potential of ammonia and the dose required to develop it (fig.3.14). Again the temperature profile conforms to the general pattern, there being no sign of surface reaction up to 200°C.

3.4.5. Inter-addition of nitrogen

Only one experiment (≠73) has been performed but there is no reason to doubt its results, which are shown in fig.3.15. Unlike the inter-addition of hydrogen there was no initial decrease. The film at 195°K had adsorbed 2×10^{17} molecules of ammonia giving a surface potential of +1.0 V and the addition of 2×10^{18} molecules of nitrogen increased the surface potential to +1.5 V (i.e. ΔS.P. of + 0.5). A further 3×10^{17} molecules of ammonia raised the surface

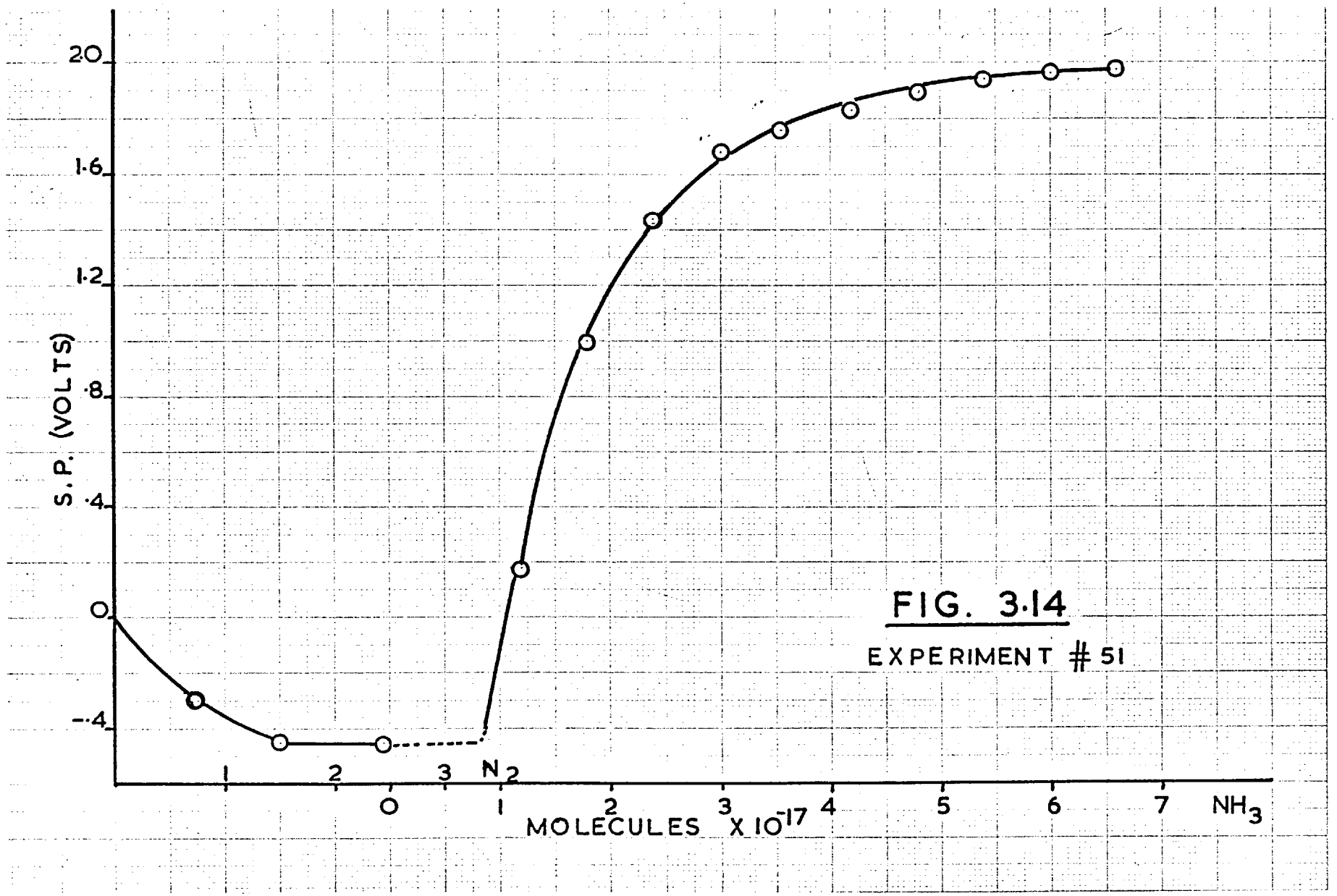


FIG. 3.14

EXPERIMENT # 51

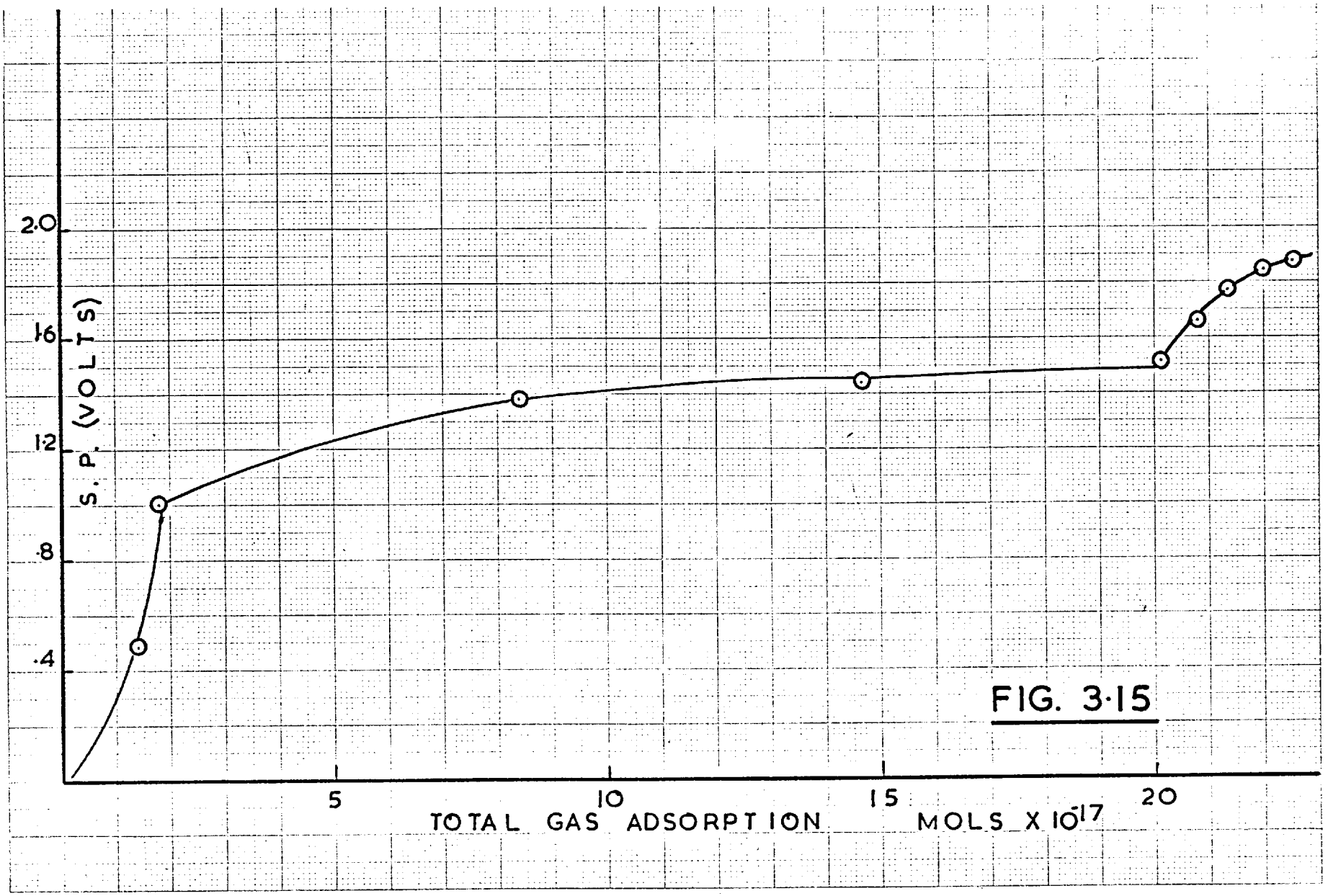


FIG. 3·15

potential to +1.86 V. Thus the formed surface potential is the same as expected on a clean film.

3.4. Surface potential of N_2 and H_2 together

In an early experiment hydrogen was added to a tungsten film at 77°K to give the maximum surface potential of -0.55 V. Excess hydrogen was added to the cell to give a pressure of ca 1 x 10^{-4} torr. After a short pumping step the surface potential was measured as -0.25 V. This suggests some physically adsorbed hydrogen had not been removed. Addition of nitrogen gave a surface potential of +0.05 V which was returned to -0.25 V on pumping which again suggests a physically adsorbed nitrogen species rather than a chemisorbed species.

A number of experiments were later performed to investigate the interaction of these two gases.

In experiment ≠103 1.4 x 10^{17} molecules of N_2 at 90°K gave a surface potential of -0.14 V, an additional 3.4 x 10^{17} molecule of H_2 increased the surface potential to -0.24 V. This is very much lower than the normal H_2 surface potential of -0.5 V on a clean film. Warming to room temperature slightly increased the surface potential to -0.37 V. The temperature was increased and finally reached 366°K but the surface potential did not change over the 2 hours of deviation. In experiment ≠104 the film was saturated with nitrogen (2.4 x 10^{18} molecules) at 195°K and gave a surface potential of 0.5 V. Hydrogen was then added to a pressure of

4×10^{-7} torr and 2×10^{18} molecules of hydrogen were adsorbed. After pumping, the surface potential was -0.53 V. This became less negative on heating, a few per cent of the hydrogen was evolved. At 290°K the surface potential was -0.1 V and reached +0.04 V at 355°K.

It is interesting to note that following this ammonia was added at 195°K and gave a surface potential of +1.8 V. In experiment #105 4×10^{17} molecules of hydrogen were adsorbed on the film to give a surface potential of -0.27 which increased to -0.37 V when 2.3×10^{17} molecules of nitrogen were added. (These quantities were sufficient in both cases to develop the maximum surface potential.) Warming to 290°K gave a surface potential of -0.4 V. Again addition of ammonia at 195°K produced a surface potential of +1.85 V. Nitrogen was added to saturate the film at 195°K with no surface potential change. It appears that the ammonia surface potential is unaffected by hydrogen and nitrogen separately or in the presence of each other.

CHAPTER 4

THE EVOLUTION OF HYDROGEN FROM ADSORBED AMMONIA

In surface potential measurement experiments it had been observed that when the ammonia coverage was high, hydrogen was evolved on warming the film. As the kinetics of this desorption should throw light on the mechanism of ammonia decomposition, detailed studies were undertaken.

It was readily established that the gas evolved was solely hydrogen by comparing simultaneous McLeod and Pirani gauge readings with the Pirani calibrations for H_2, N_2 and mixtures thereof. These readings were sensitive to the presence of a nitrogen content of 5% and probably less. Frangenberger[10] and others have similarly found hydrogen to be the only product of the catalytic decomposition of ammonia on tungsten powders.

Method

In these kinetic experiments the film was prepared as before and dosed with ammonia. As here larger quantities of ammonia were involved than in surface potential experiments, the gas trapped between BC (fig.2.1) was expanded into CD and C raised again. Then the total dose was admitted to the cell by lowering D. Throughout this, the mercury in E was kept at the upper reference mark. In calculating the amount of gas adsorbed, allowance for the "dead space" of the dosing system was made. When the adsorption was complete the mercury in F was raised to the fixed mark to isolate

the dosing system when hydrogen was evolved. Hydrogen evolution was studied with the traps at liquid oxygen temperature (see later).

The cell used had the same dimensions as the surface potential cell but without the emission filament well and platinum foil. The pressure in the apparatus was converted to molecules using

$$n = \frac{p}{R} \sum \left(\frac{V}{T}\right)_i$$

where V_i was the volume of that section of the apparatus at $T_i\,^{\circ}K$. As an evolution experiments the only variable was the cell temperature

$$n = p \times f\ (T_{cell}).$$

Figure 4.1 shows the value of f for varying cell temperature.

Preliminary experiments

In early experiments it was established that at temperatures lower than $273^{\circ}K$ no hydrogen was evolved but a small quantity of ammonia was. Thus at $251^{\circ}K$ 4×10^{14} molecules were evolved and this evolution was completed in 20 mins. The ammonia was readsorbed on cooling to $195^{\circ}K$. To remove this small amount of ammonia in later experiments the traps were cooled by liquid oxygen. This had the added advantage of protecting the film from mercury contamination more effectively than CO_2/alcohol; thus the experiments could be extended over two days. This was necessary as the hydrogen evolution generally took about 8 hours for "completion" at a given temperature.

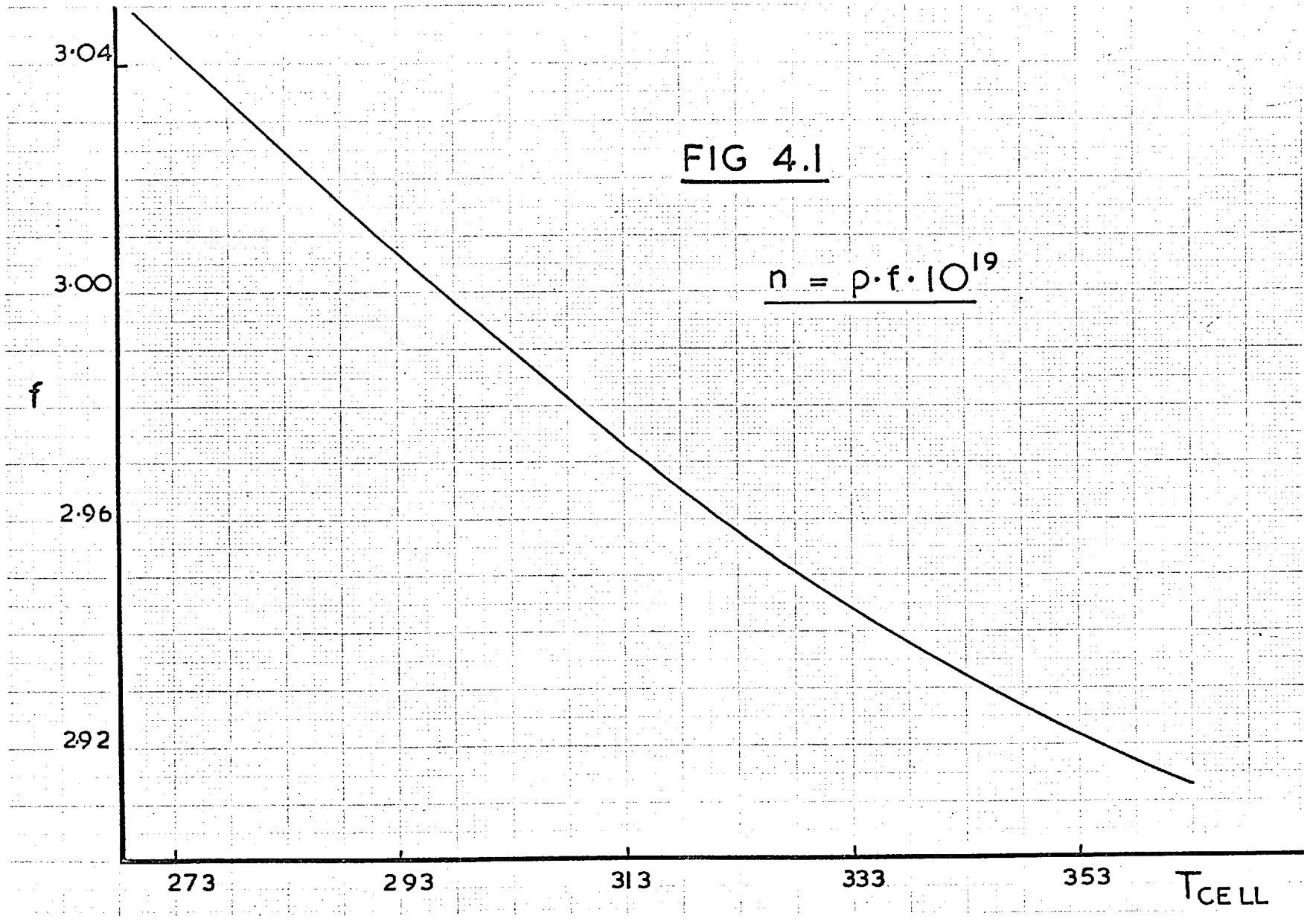


FIG 4.1

$n = \rho \cdot f \cdot 10^{19}$

In another preliminary experiment (≠ 111) the pressure of hydrogen evolved at 273°K was 6.5×10^{-3} torr after 270 mins. When the film was cooled to 195°K the pressure dropped to 0.5×10^{-3} torr in 10 mins. Warming back to 273°K caused the pressure to return to 6.5×10^{-3} torr within a few minutes. This was pumped away and the temperature increased to 291°K. In 75 mins. the pressure reached 4.75×10^{-3} torr and dropped to less than 10^{-6} torr within 10 mins. when the film was returned to 195°K. This reversible hydrogen process was a universal feature of these experiments and a more detailed study will be described later.

Experiment ≠ 117

In this experiment the film was dosed with ammonia at 195°K, the final dose gave a pressure of 6.5×10^{-3} torr which fell to 4.8×10^{-3} in 1 hour. A total of 5.35×10^{18} molecules were adsorbed. The ammonia not adsorbed was pumped off and the traps changed from CO_2/alcohol to liquid oxygen. The cell temperature was raised to 273°K and the pressure build up observed over a period of 6 hours. When the hydrogen had been pumped off (pumping time ca 5 mins) the cell was raised to 291°K; this procedure was repeated for temperatures of 307°K and 328°K. Figure 4.2 shows the pressure increase with time for these four temperatures (328°K is shown separately for clarity). The pressure readings were taken with the Pirani until p rose above the limit of the Pirani (ca 9×10^{-3} torr). From time to time McLeod readings were taken to establish that the gas was indeed hydrogen and, in later experiments,

when this had been established, such readings served as a check on the constancy of the Pirani calibration.

Before pumping off the hydrogen in each temperature step (T_i) the film temperature was lowered to 195°K whereupon some of the hydrogen was readsorbed. The time for completion of the process appeared to be less than the time required for the cell to reach thermal equilibrium (i.e. a few minutes). When the cell temperature was returned to T_1°K this hydrogen was evolved again within the thermal equilibrium period. In table 4.1 the data from these experiments is given. At 307°K the reversible process was examined at various temperatures and the same rapidity was found.

Table 4.1

Temperature step °K	H_2 evolved $n = 10^{17}$ molecules	$\sum n_i \times 10^{17}$	Temperature of readsorption	H_2 readsorbed $n_i \times 10^{17}$
273	3.38	3.38	195	1.78 at $p = 4.9\times10^{-3}$
291	2.82	6.20	195	1.65 at $p = 9.4\times10^{-3}$
307	2.21	8.41	286	0.19
			273	0.96
			195	2.16 at $p = 1.4\times10^{-4}$

The rapidity and reversibility of this process shows that the hydrogen was weakly adsorbed. Following the desorption at 328°K the film was held at 348°K for 17 hours. The hydrogen evolved

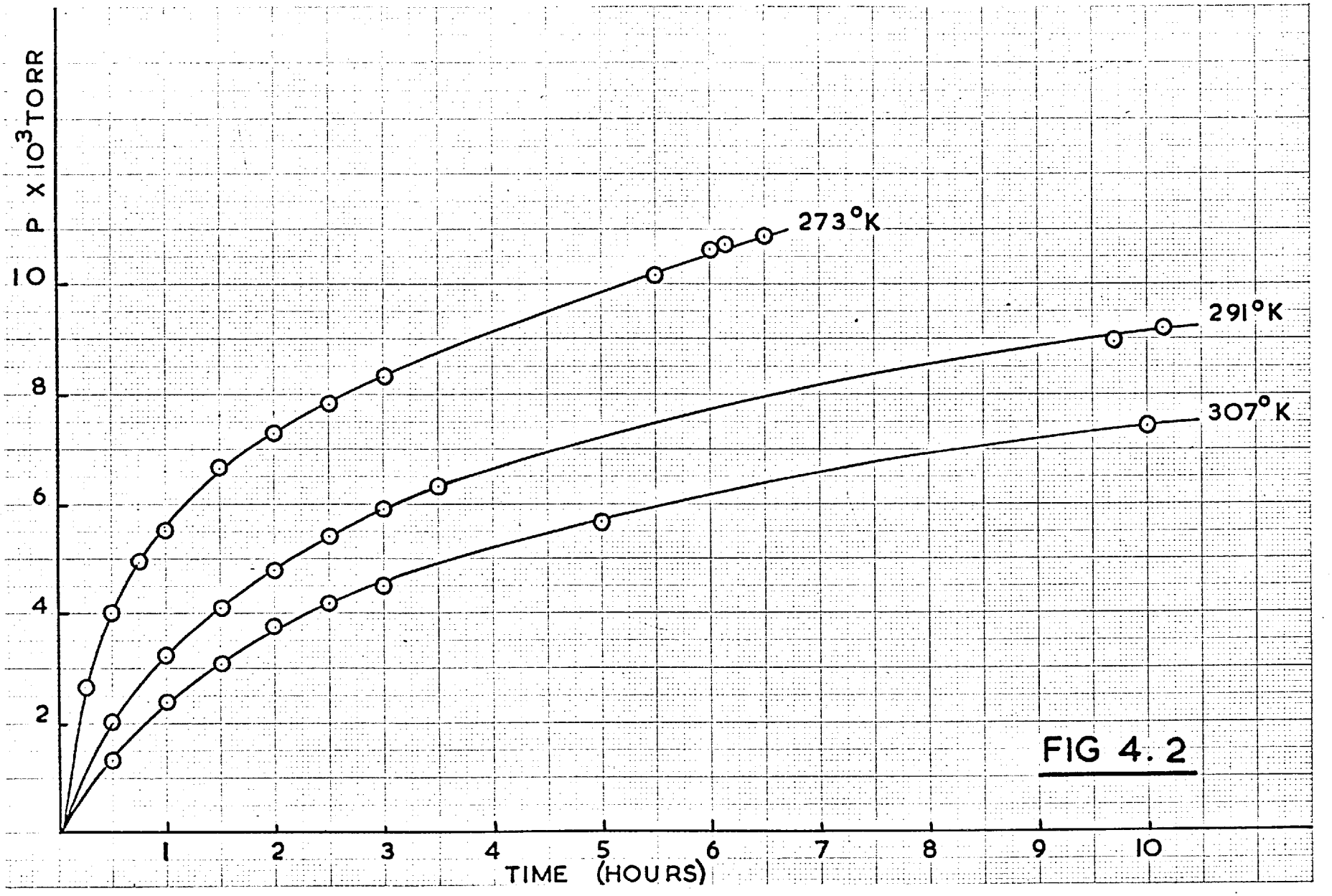


FIG 4.2

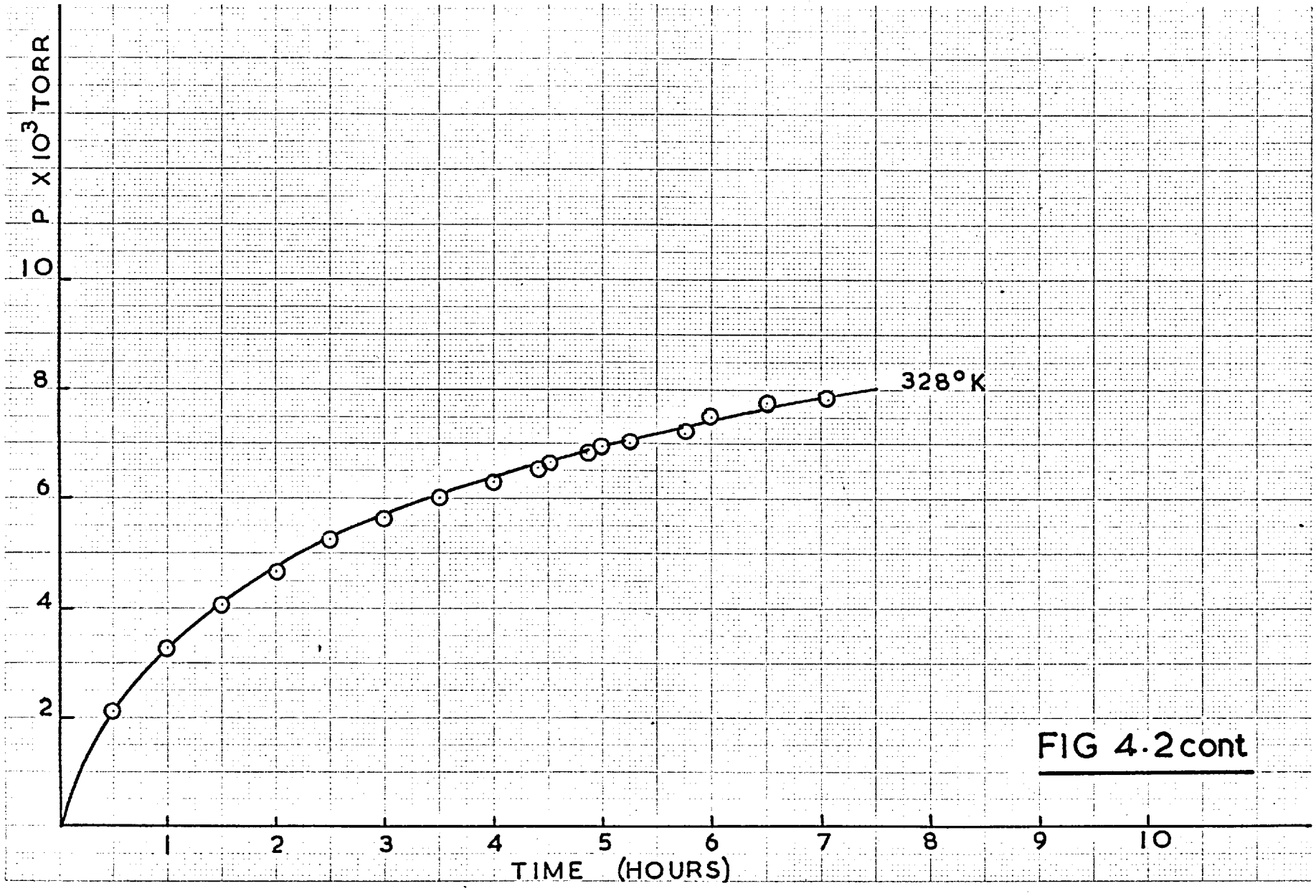


FIG 4.2cont

(ca 2 x 10^{17} molecules) was pumped away. At this stage the traps were raised from 90°K to 195°K, thus vaporizing the ammonia evolved which was a very small quantity as expected from preliminary experiments. Hydrogen was then admitted to the cell and isotherms measured over a limited range, these are shown in fig.4.3 From this an isosteric log p vs $1/T^{\circ}K$ plot was drawn (fig.4.3). The heat of adsorption was found to be ca 9 kcal/mole.

Following this result an experiment (≠ 118) was performed to examine this more closely. A tungsten film was dosed at 195°K with 5 x 10^{18} molecules and, after removing the unabsorbed ammonia, heated to 348°K whereupon 1.8 x 10^{18} molecules of hydrogen were evolved over 12 hours. This hydrogen was pumped off. Isotherms were then obtained by measuring the pressure at four temperatures after each hydrogen addition. Equilibrium was obtained within five minutes of temperature changes. The isotherms and isosterics are shown in fig.4.4. At coverages above 5 x 10^{17} molecules (approximately 2 x 10^{14} molecules per cm^{-2}) the isotherms are parallel, giving an adsorption heat of ca 9 kcal/mole. Below this coverage the heat is somewhat greater than 9 kcal/mole.

Returning to experiment ≠ 117, the p/t relationship was analysed as a second order process. A second order reaction is characterised by the equation

$$t = \frac{1}{k(a-x)} - \frac{1}{ka}$$

where k is the second order velocity constant, a the initial

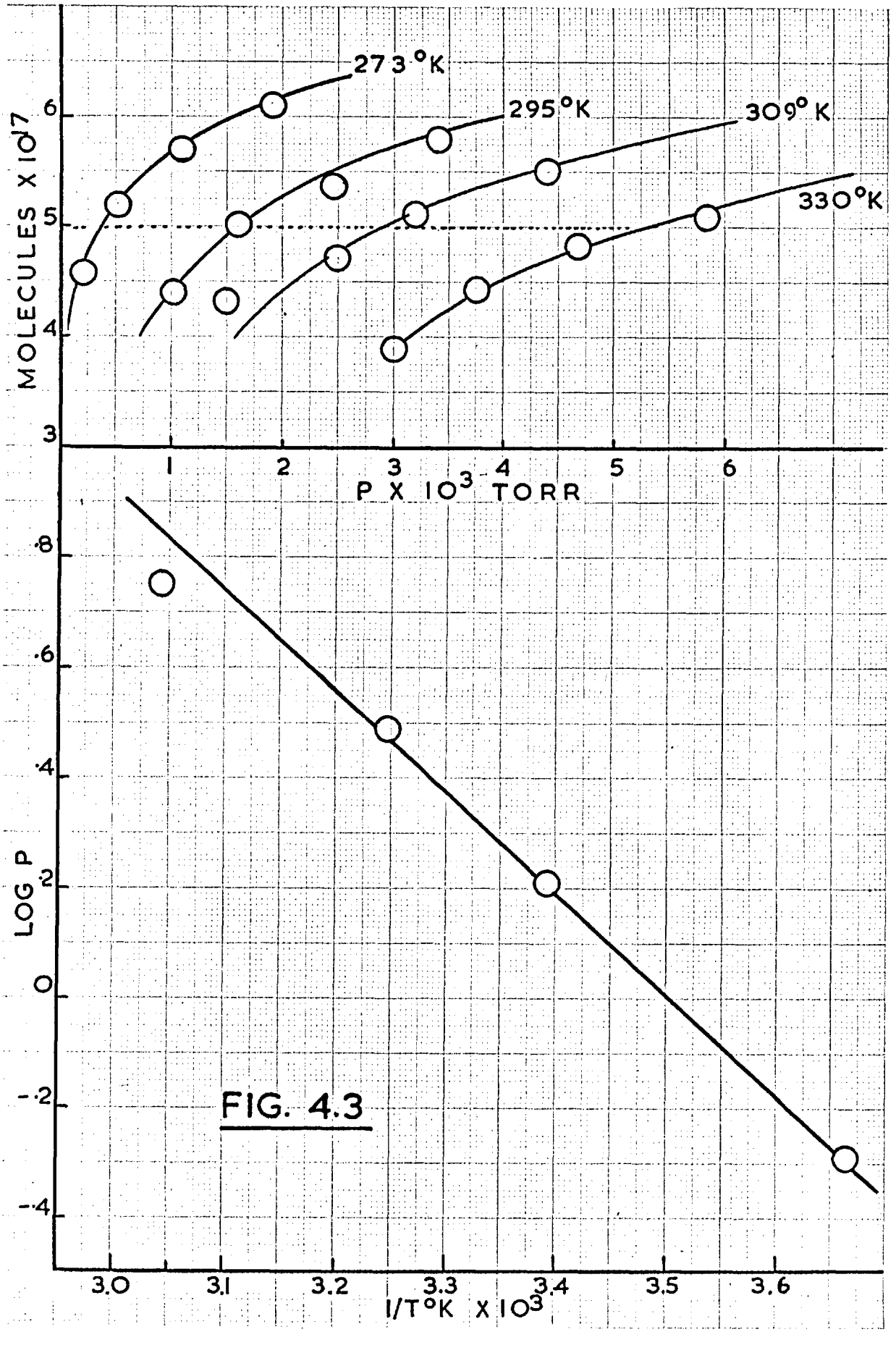

273°K
295°K
309° K
330°K
MOLECULES X 10^17
6
5
4
3
1
2
3
4
5
6
P X 10^3 TORR
LOG P
·8
·6
·4
·2
0
-·2
-·4
3.0
3.1
3.2
3.3
3.4
3.5
3.6
1/T°K X 10^3

FIG. 4.3

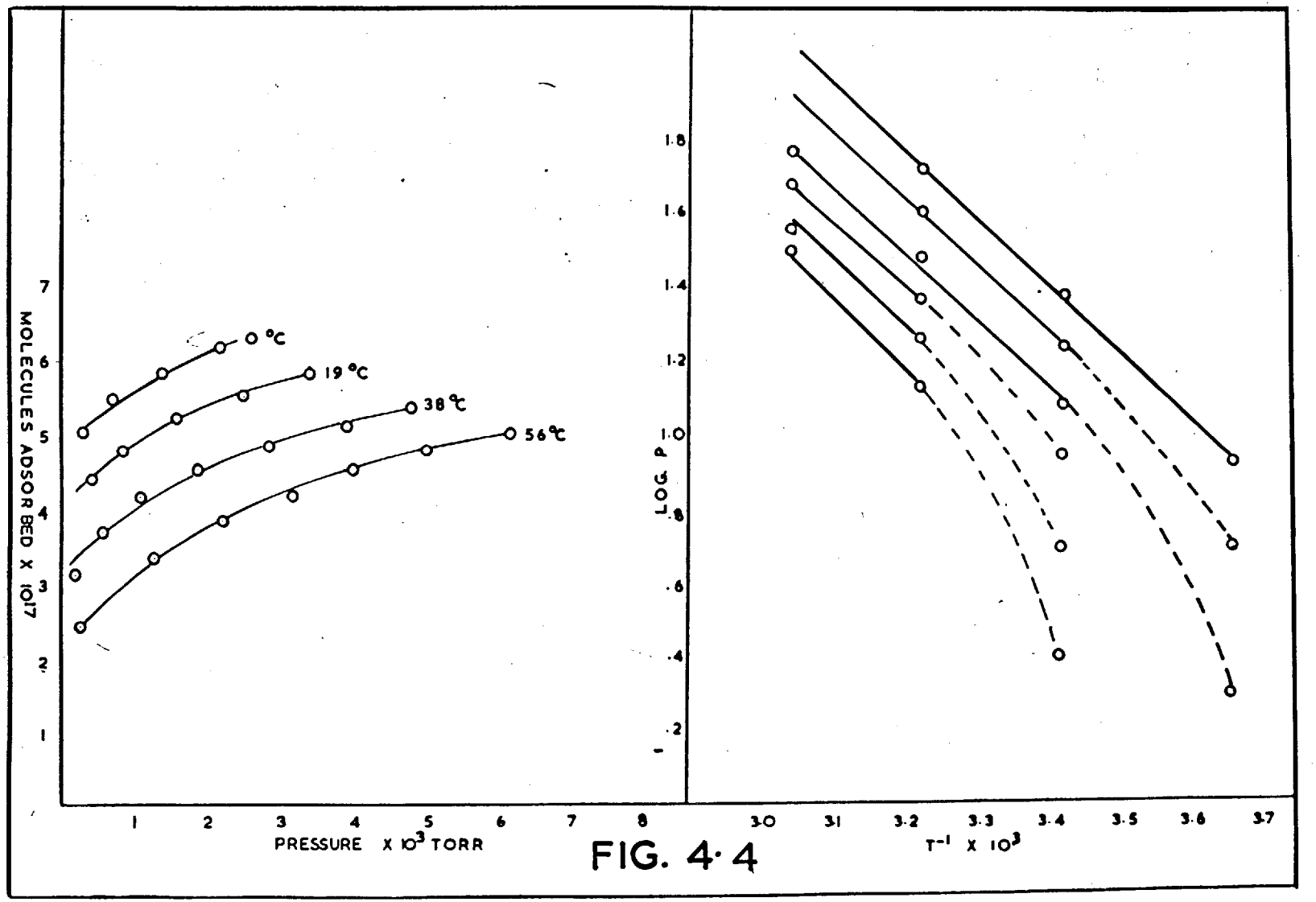

MOLECULES ADSORBED X 10^17
PRESSURE X 10^3 TORR
0 °C
19 °C
38 °C
56 °C
LOG P
T^-1 X 10^3

FIG. 4·4

concentration, x the amount reacted after time t. In this case $x = p_t$ and $a = p_\infty$. The latter was found by extrapolation. Figure 4.5 shows the plot of $1/(p_\infty - p)$ for the desorption at 273°K; similar plots were obtained for the other temperatures. The deviation from the straight line at the beginning of the desorption was not found at temperatures above 273°K. Although the kinetics are apparently in accord with a second order mechanism the activation energy obtained from a plot of log k against 1/T gave an apparent activation energy of 2 kcal $mole^{-1}$. This is a totally unacceptable value. A simple velocity equation for the rate of desorption, u, has been given by Polanyi and Wagner[195] as

$$u = \nu . n_s \theta . \exp\left[\frac{-E}{RT}\right] \qquad 4.1$$

This is based on the assumption that any particle, possessing the requisite activation energy E, will be desorbed within the period of one vibration perpendicular to the surface. The frequency of this vibration is ν and for a chemical bond has a value of ca 10^{13} sec^{-1}. The term n_s is the number of sites available for adsorption and θ the fraction of these occupied. Tamaru[75] has given the number of sites per cm^2 as 1.22×10^{15} for tungsten. Thus the initial rate of desorption would be

$$u = 10^{13} . 1.2 \times 10^{15} \times \exp\left(\frac{-2 \times 10^3}{2 \times 273}\right)$$

$$\simeq 10^{27} \text{ molecules } sec^{-1} \text{ } cm^{-2}.$$

This value would give rise to an explosive desorption. At 273°K the initial measured rate was about 3×10^{10} molecules $sec^{-1} cm^{-1}$.

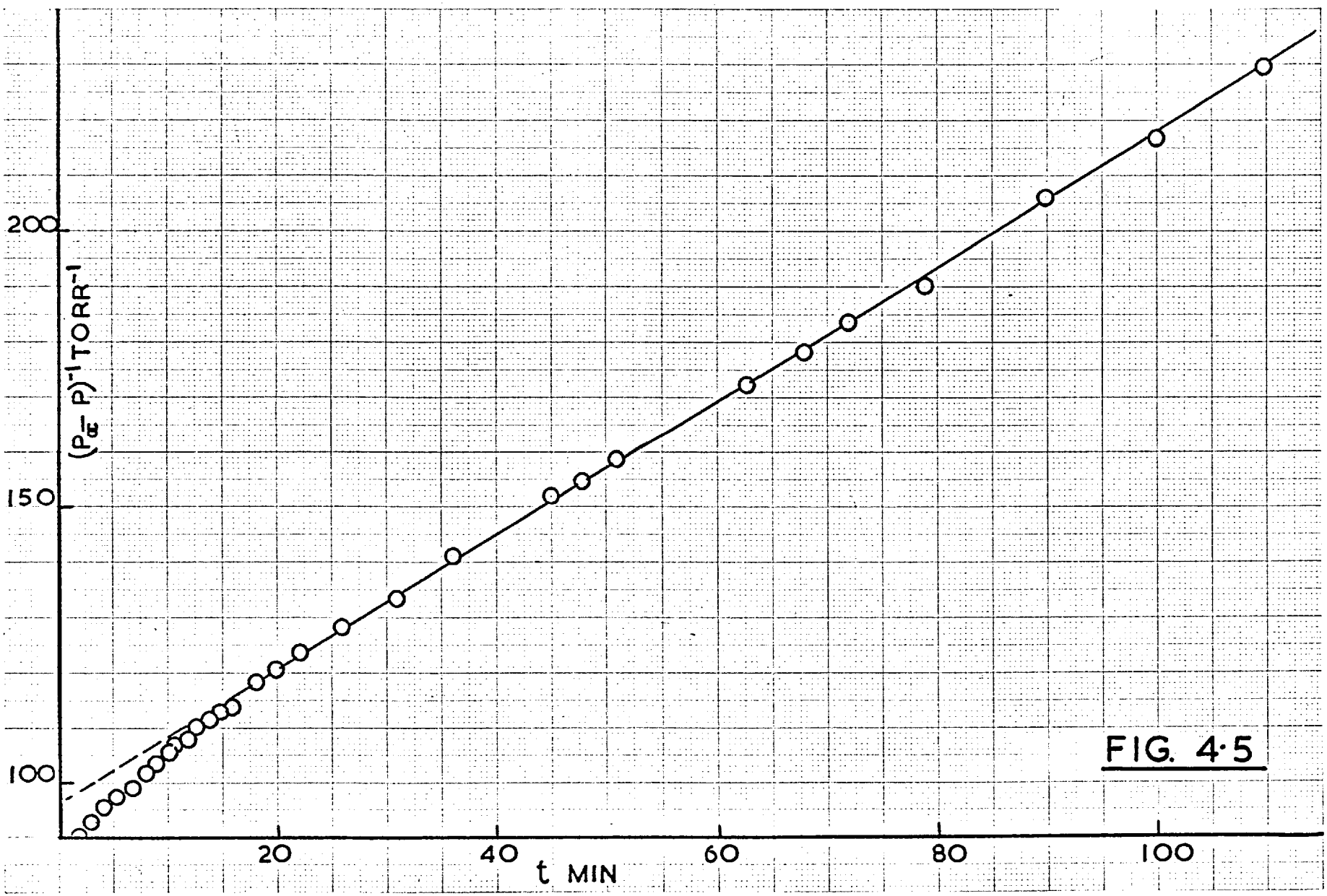


FIG. 4·5

Thus, although the data of this and of subsequent experiments could be fitted to a second order equation for each temperature, the conclusion is fallacious.

If n_1 molecules of hydrogen were evolved at 273°K and a further n_2 molecules at 291°K it is reasonable to assume that had the film been initially warmed to 291°K then the number of molecules evolved would have been $(n_1 + n_2)$. A plot of $\sum_1^i n_i$ against T_i is shown in fig.4.6. The linear relationship indicates that an Elovich[190] treatment of the results is appropriate. The Elovich theory considers the desorption activation energy E_d to increase as the number of molecules desorbed (q) increases :

$$E_d = E_o + \alpha q \qquad 4.2$$

where α is a constant. The rate of desorption is given approximately by[61]

$$\frac{dq}{dt} = \frac{RT}{a\alpha} \exp - \frac{(E_o + \alpha q)}{RT} \qquad 4.3$$

where a is a constant. Integration of eqn.4.3, applying the boundary condition q = 0 when t = 0, gives

$$\ln (t + a \exp E_o/RT) = \ln a + (E_o + \alpha q)/RT \qquad 4.4$$

or

$$\ln (t + t_o) = \ln a + (E_o + \alpha q)/RT \qquad 4.5$$

For equal values of $\ln (t + t_o)$:

$$(E_o + \alpha q_1)/T_1 = (E_o + \alpha q_2)/T_2 \qquad 4.6$$

whence

$$(E_o + \alpha q_i)/T_i = \text{constant.}$$

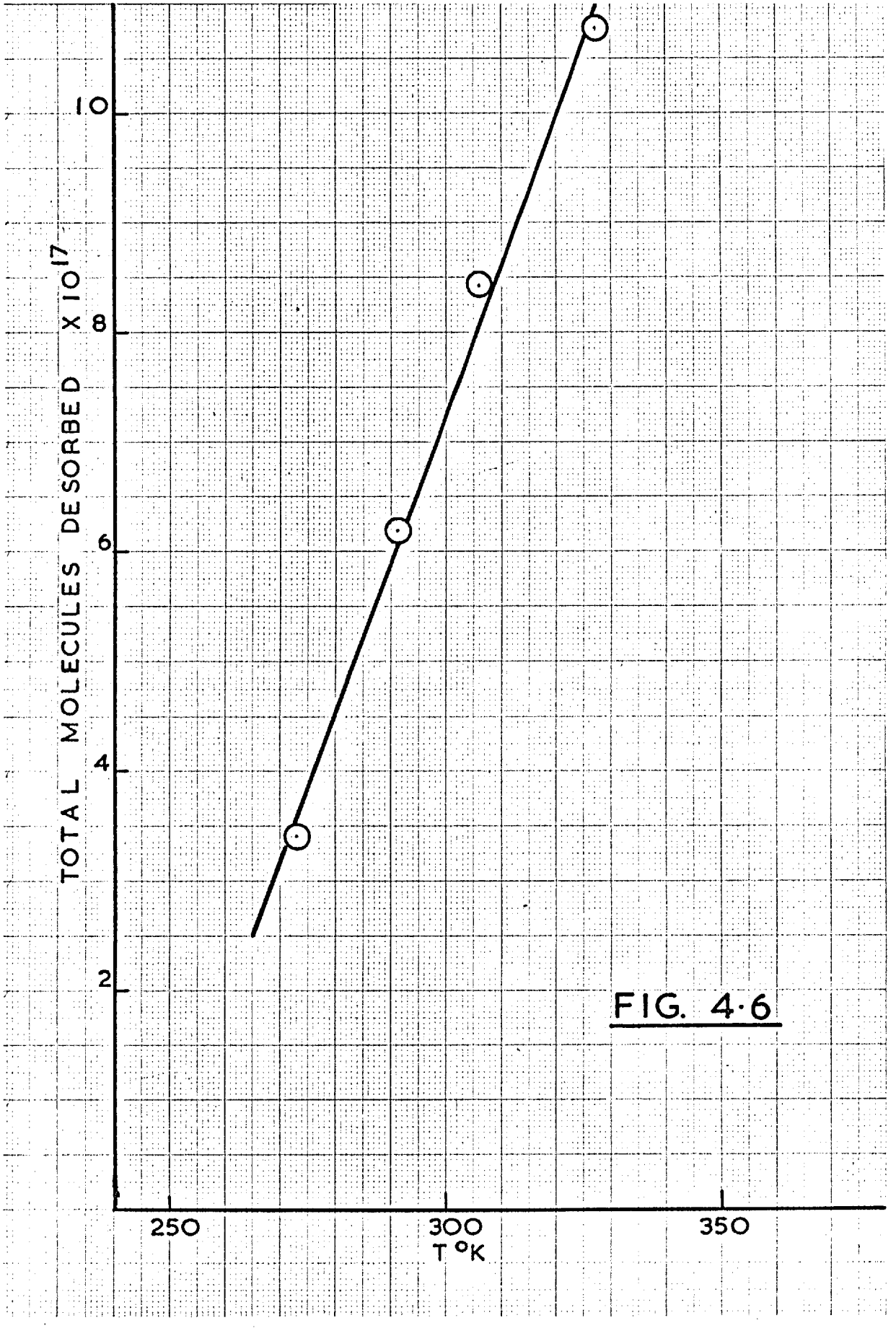


FIG. 4·6

This condition will be true also if t is very large for after such a time the rate of desorption will not be appreciable. Therefore a plot of q_i against T_i should be linear if the desorption is governed by Elovichian kinetics.

The results of an interesting, but not too definitive, experiment are shown in fig.4.7. A film having a layer of ammonia was subjected to a temperature linearly dependent upon time. It will be seen that the pressure rose linearly with time in step with the temperature rise.

The theory is also applicabke to adsorptive and desorptive on uniform and non-uniform surfaces[159] and it may also be derived[196][197] if the total number of surface sites is not constant but is a function of both the quantity of gas adsorbed and the temperature. In these cases it must also be assumed that the rate of adsorption is governed by the number of available sites, which number must diminish exponentially as the amount adsorbed increases. This implies that chemisorbed molecules de-activate sites in excess of actual occupany.

Writing equation 4.3 as

$$\frac{dq}{dt} = a \exp(-\beta q)$$

from which it will be seen that

$$\frac{\log (dq/dt)}{q} = \left(\frac{\partial E}{\partial q}\right) \cdot \frac{1}{2.303\ RT} \qquad 4.7$$

Plots of log (dp/dt) against p are shown in fig. 4.8 and 4.10. Table 4.3 summarises the information obtained therefrom.

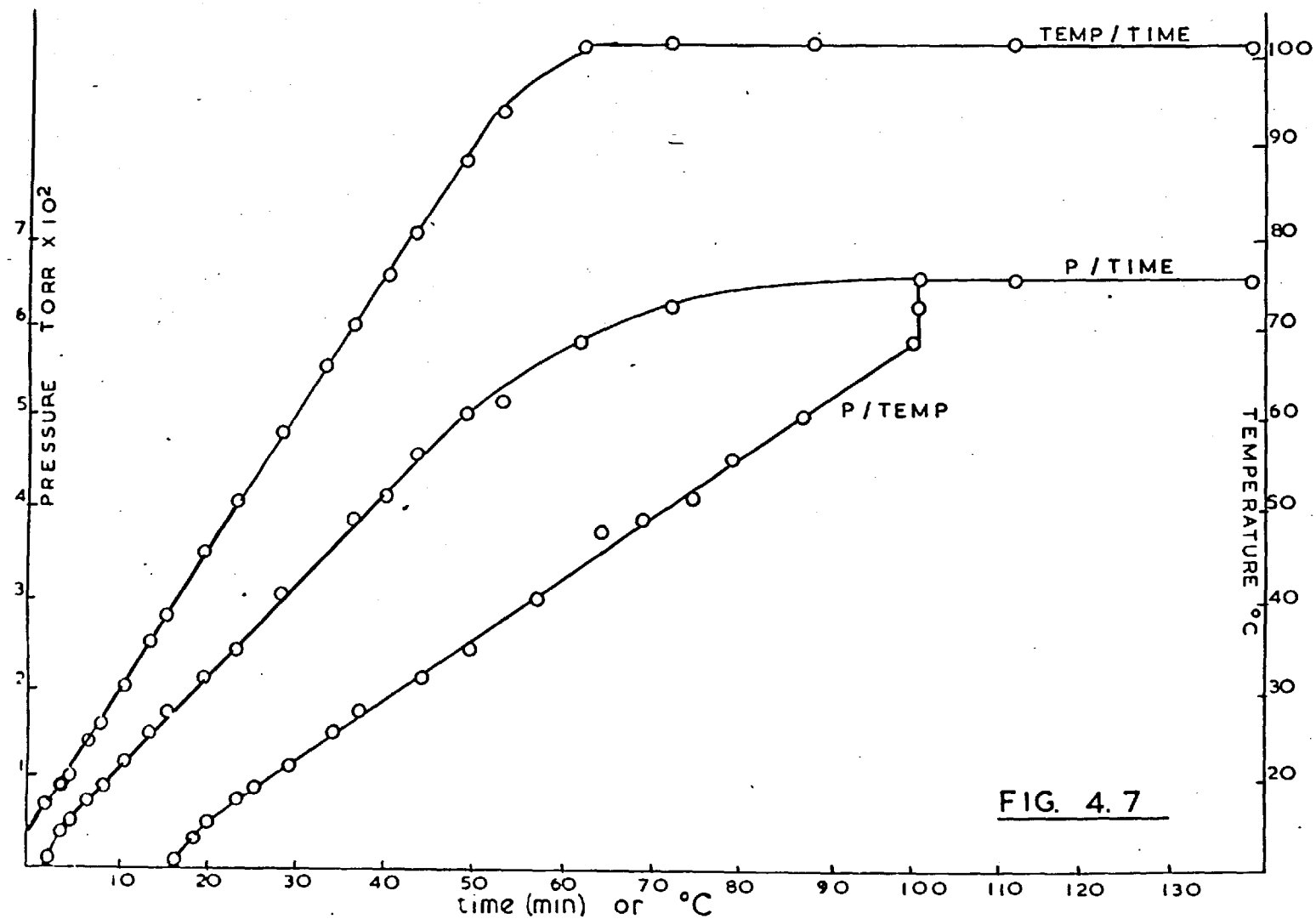

TEMP / TIME
P / TIME
P / TEMP
PRESSURE TORR X 10²
TEMPERATURE °C
time (min) or °C
1
2
3
4
5
6
7
10
20
30
40
50
60
70
80
90
100
110
120
130
20
30
40
50
60
70
80
90
100

FIG. 4.7

FIG. 4·8

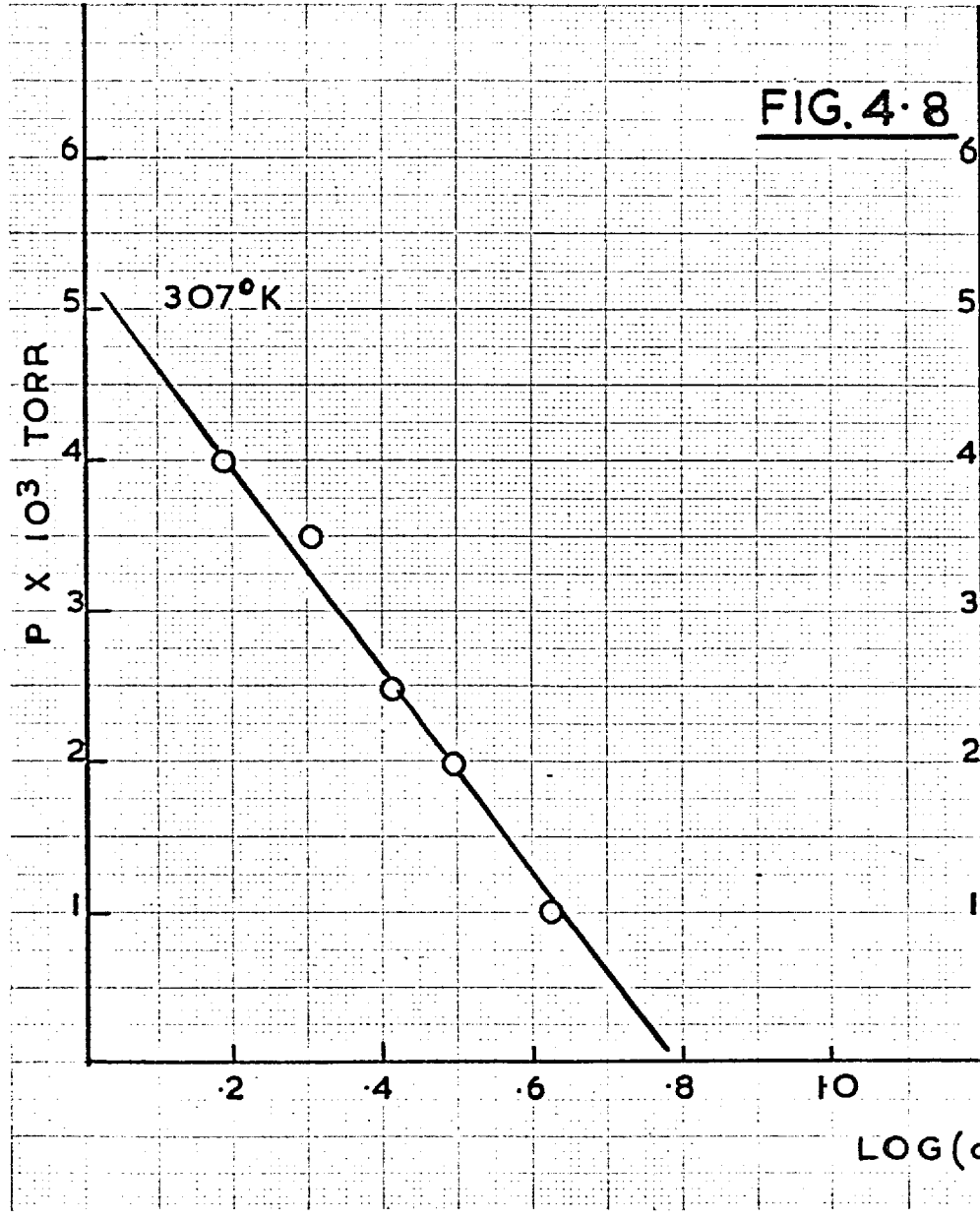
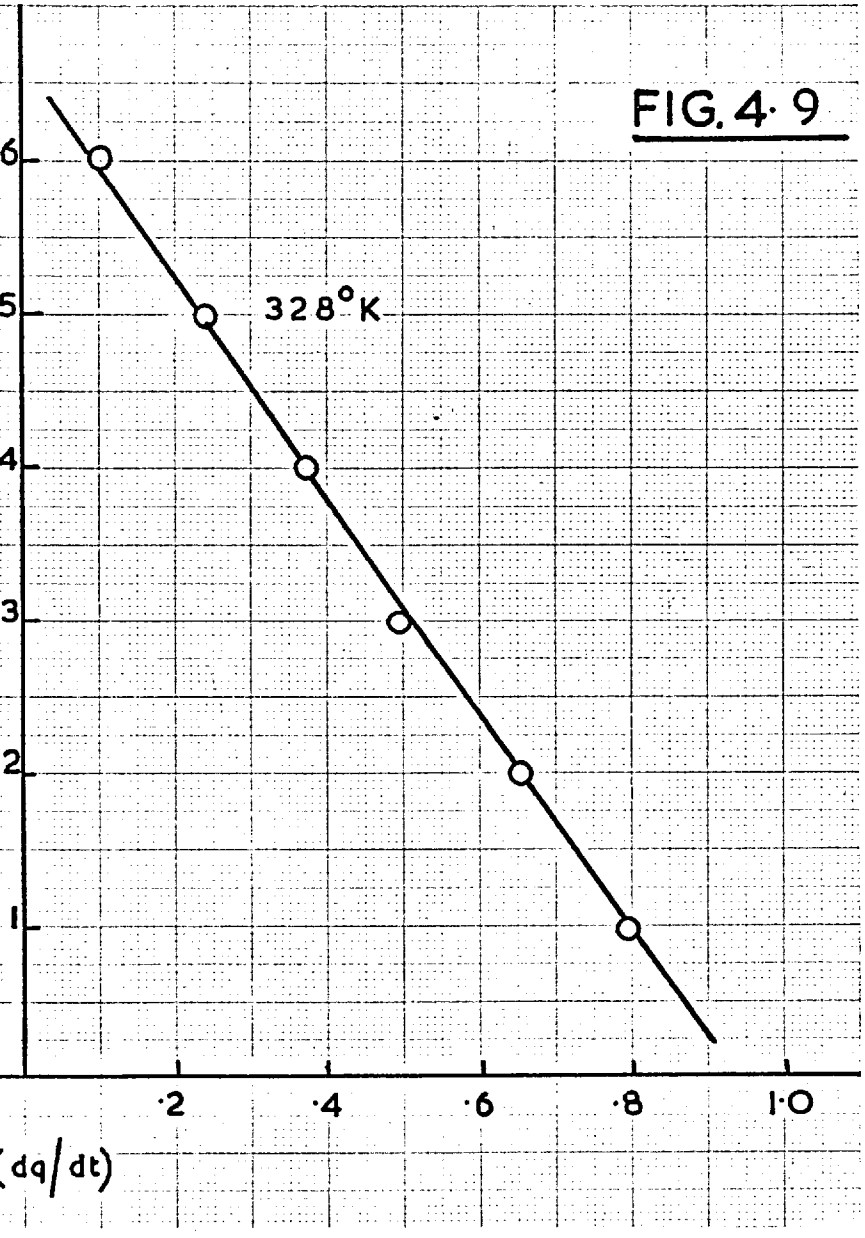


FIG. 4·9



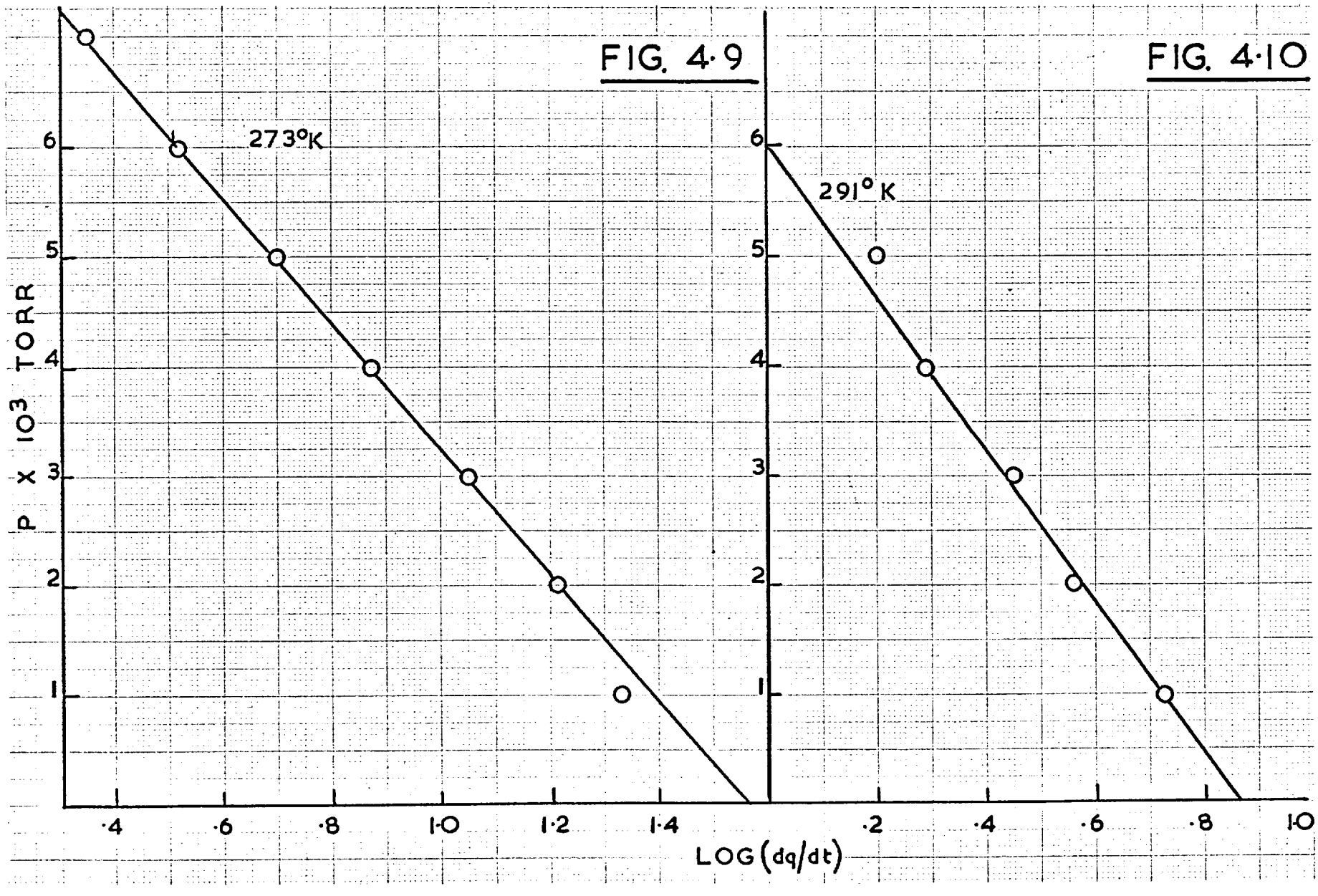


FIG. 4·9
FIG. 4·10
27.3°K
291° K
P X 10³ TORR
1
2
3
4
5
6
·4
·6
·8
1·0
1·2
1·4
·2
·4
·6
·8
1·0
LOG (dq/dt)

Table 4.3

T	$\frac{\log dp/dt}{p}$	$\frac{\log dq/dt}{q} = f$	$f \times 4.6 = f'$	$f' \times T = \left(\frac{\partial E}{\partial q}\right)$
273	$\frac{1.21}{7\times10^{-3}} = 1.73\times10^{2}$	5.69×10^{-18}	2.62×10^{-17}	7.15×10^{-15}
291	$\frac{0.70}{5\times10^{-3}} = 1.40\times10^{2}$	4.66×10^{-18}	2.15×10^{-17}	6.24×10^{-15}
307	$\frac{.318}{2.5\times10^{-3}} = 1.32\times10^{2}$	4.43×10^{-18}	2.04×10^{-17}	6.25×10^{-15}
328	$\frac{.428}{3\times10^{-3}} = 1.41\times10^{2}$	4.78×10^{-18}	2.20×10^{-17}	7.22×10^{-15}

The average value of $(\partial E/\partial q)$ is 6.45×10^{15} cal.mole^{-1} molecules^{-1}.

Eqn.4.5 predicts that a plot of log $(t + t_o)$ against q should give a straight line. In fig.4.11 to 4.14 such plots are shown and they are linear. This is confirmation of the applicability of the Elovich treatment. The slope of these plots is $2.303\ RT/(\partial E/\partial q)$ and the average value was 6.52×10^{-15} cal^{-1}mole^{-1} molecules^{-1}, in good agreement with the above method of evaluation.

We shall now consider the relationships which may be derived from a heterogeneous surface assuming second order kinetics and an activation energy increasing monotonially with q, the amount desorbed. As a model we use a surface having n patches, each with an initial population of a and let the energy separation of each patch be ΔE. For any one patch the desorption will follow

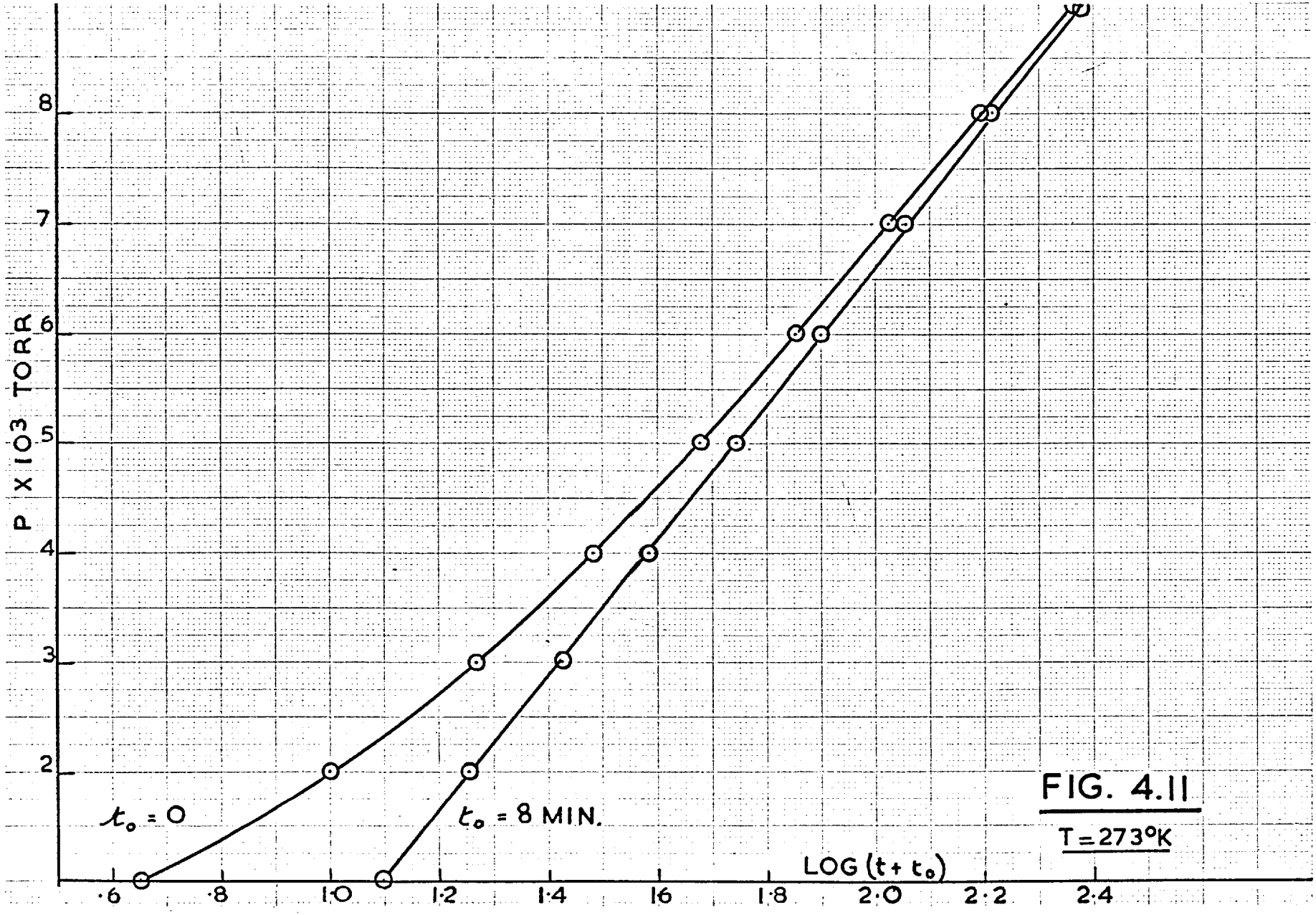


FIG. 4.11

T = 273°K

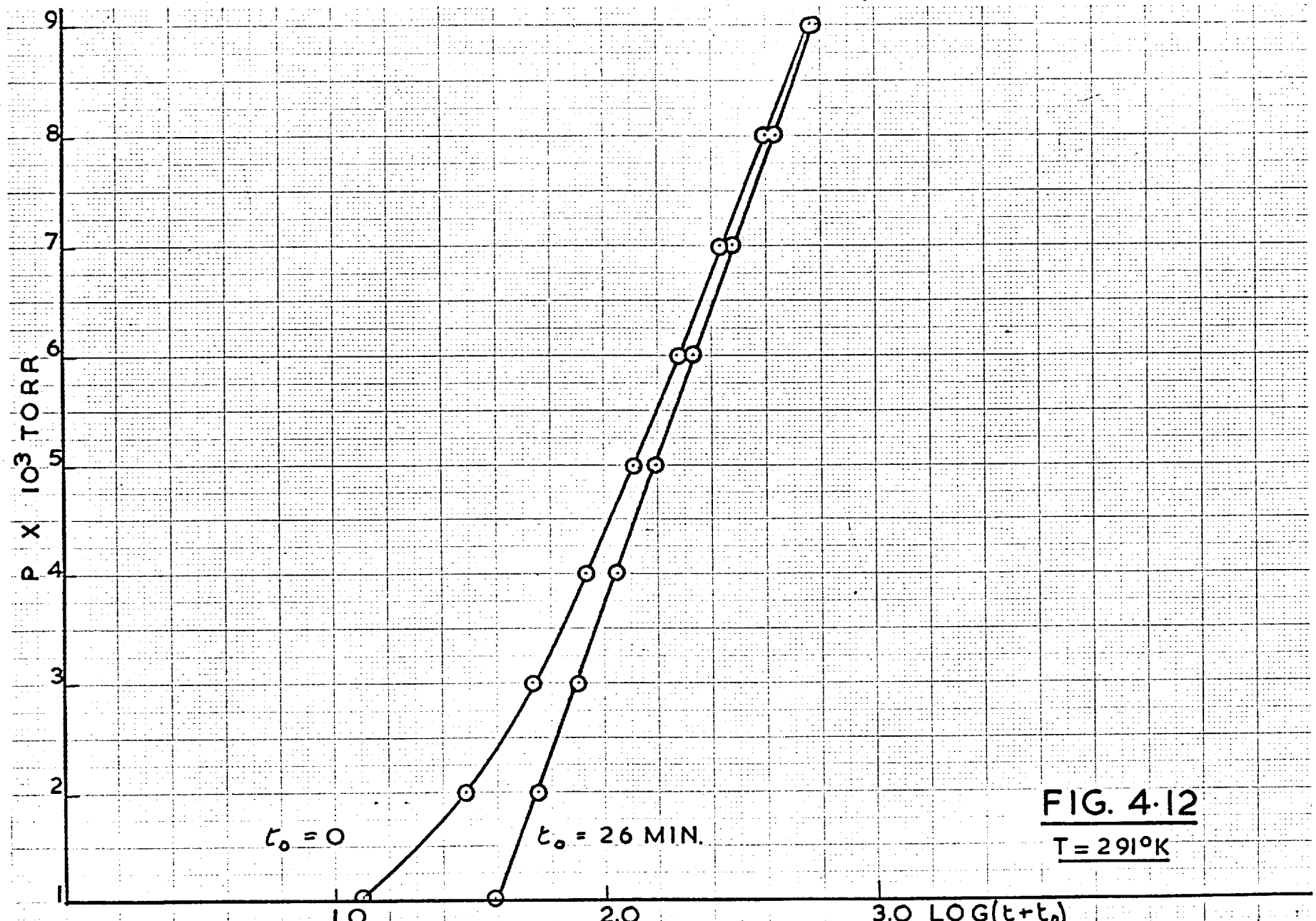


FIG. 4·12

T = 291°K

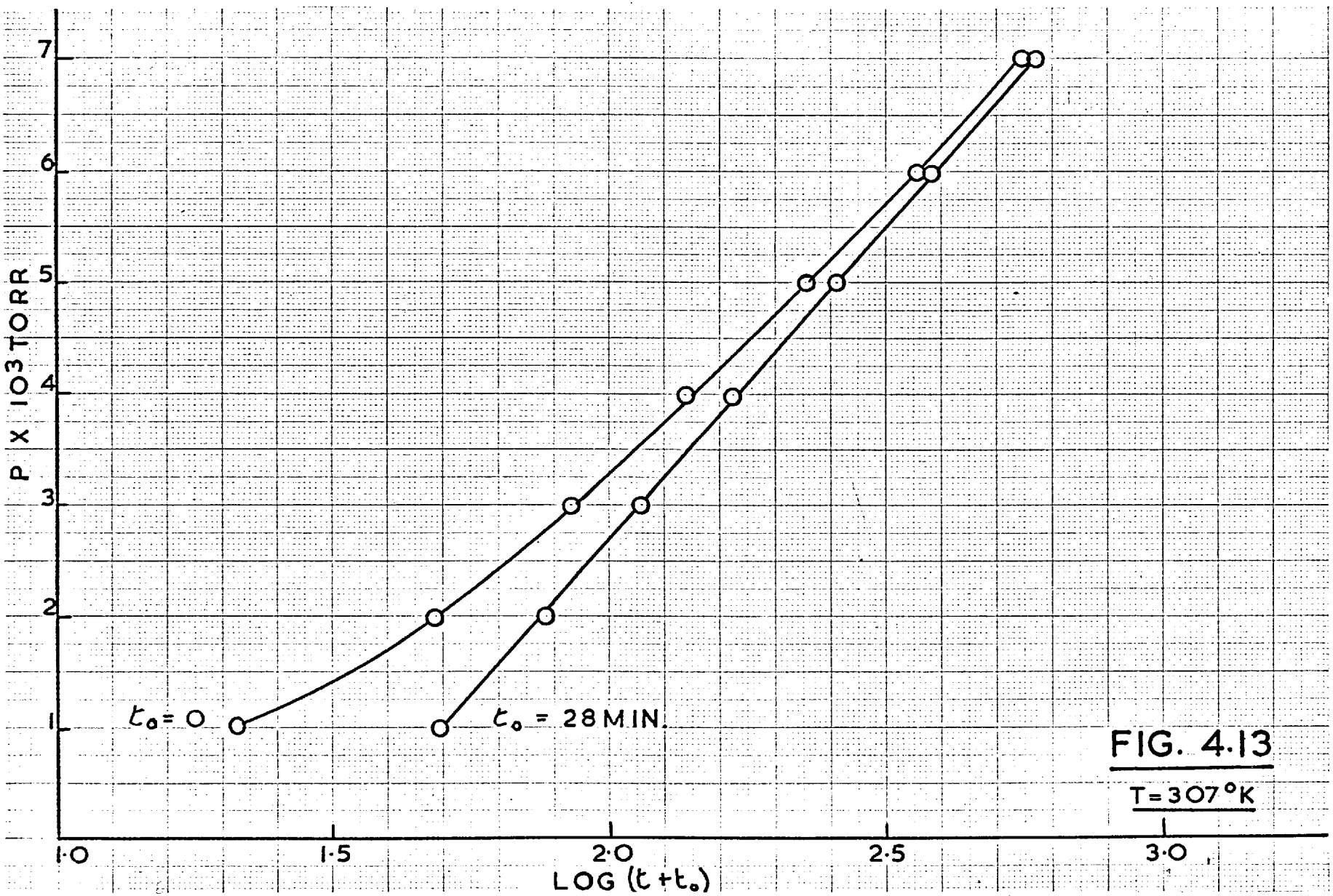


FIG. 4.13

T = 307 °K

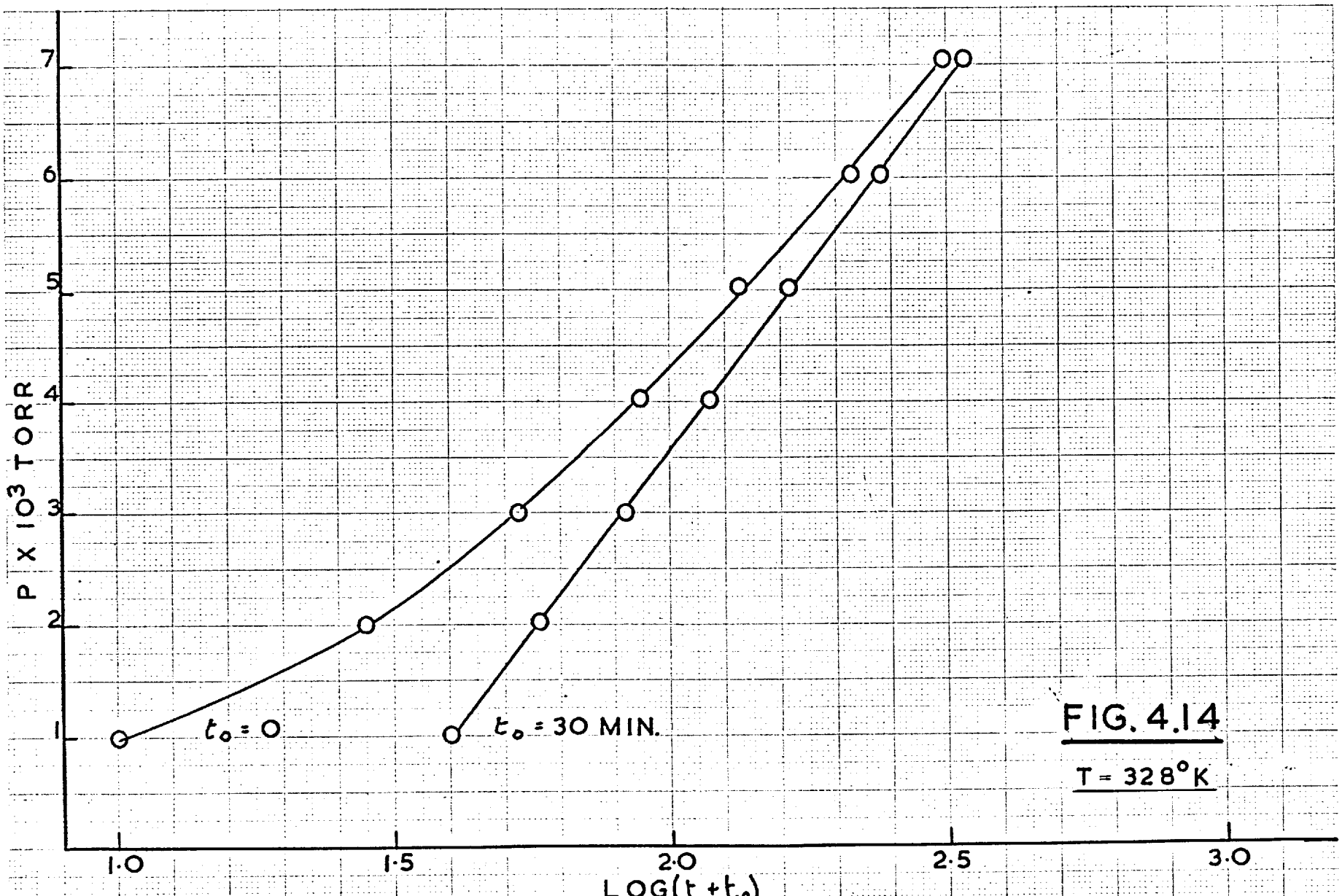


FIG. 4.14

T = 328°K

$$\frac{dx}{dt} = k\ (a-x)^2$$

where $k = C \exp\left(-\frac{E}{RT}\right)$ and if we are considering the ith patch

$$k = C \exp - \left[\frac{E_o + i\ \Delta E}{RT}\right]$$

$$= C \exp - \left(E_o/RT\right) \exp - \left(i\Delta E/RT\right)$$

$$= B \exp - \left(\frac{i\Delta E}{RT}\right)$$

Thus after time t the ith patch will have desorbed xi molecules where :

$$x_i = at\left\{\frac{k_i}{k_i t + 1/a}\right\}$$

For the entire surface the number of molecules desorbed will be

$X = \sum x_i$.

$$X = at \sum_i \frac{k_i}{k_i t + 1/a}$$

or

$$X = at \int \frac{k_i\ d_i}{k_i t + A}$$

$$= at \int \frac{P \exp\left(\frac{i\Delta E}{RT}\right)}{B \exp\left(\frac{i\Delta E}{RT}\right) + A}\ di$$

If y is put equal to $\exp - \left(i\Delta E/RT\right)$ this reduces to

$$X = -\int \frac{BRT}{\Delta E\ (Bty + A)}\ dy$$

$$\therefore X_t = -\frac{at\ BRT}{\Delta E}\ \frac{1}{Bt}\ \left[\ln\ (Bt\ y + \frac{1}{a})\right]_o^t$$

$$= -\frac{aRT}{\Delta E}\ \left[\log\left\{t\ C \exp\left(\frac{-E_o}{RT}\right) \exp\left(\frac{-i\Delta E}{RT}\right) + \frac{1}{a}\right\}\right]_o^t$$

If the desorption continues until E_m is the activation energy of the last step affected

$$= - \frac{aRT}{\Delta E} \log \left\{ \frac{a\ Ct\ \exp\left(\frac{-E_m}{RT}\right) + 1}{a\ Ct\ \exp\left(\frac{-E_o}{RT}\right) + 1} \right\}$$

This reduces to an equation of the form

$$X_t = S \log (t + t_o) + C$$

whence

$$\left(\frac{\partial X}{\partial t}\right)_{T_j} = \frac{\partial}{dt} \left(S_i \log (t + {}_i t_o) + C \right)$$

$$\left(\frac{\partial X}{\partial t}\right)_{T_i} = \frac{S_i}{t + {}_i t_o}$$

$$\left(\frac{\partial X}{\partial t}\right)_{T_i, t_{max}} = \frac{S_i}{t_{max} + t_o}$$

Since

$$\left(\frac{\partial X}{\partial t}\right)_x = \frac{a^2 CRT}{\Delta E} \left\{ \exp -\left(\frac{E_o + \frac{x}{a} \Delta E}{RT} \right) \right\}$$

$$\frac{k_2}{k_1} = \left[\frac{S_2}{T_2} \cdot \frac{T_1}{S_1} \times \frac{{}_1 t_{max} + {}_1 t_o}{{}_2 t_o} \right] \qquad 4.8$$

but

$$\log \frac{k_2}{k_1} = \frac{E_o}{RT} \left[\frac{T_2 - T_1}{T_2 T_1} \right] \qquad 4.9$$

We may therefore use the slope S of the log $(t + t_o)$ vs q plots to obtain approximate values of E.

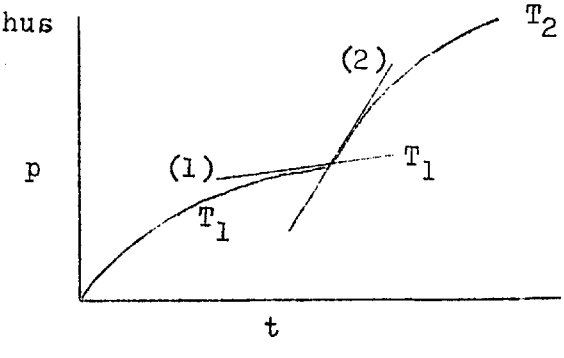
From this equation we obtained activation energies shown in table 4.4.

Table 4.4

Temperature Range ^{o}K	ΔE; kcal $mole^{-1}$	q, molecules desorbed
(a) 273/291	25.4	3.4×10^{17}
(b) 291/307	34.2	6.2×10^{17}
(c) 307/327	30.6	8.4×10^{17}

A consequence of this equation is that the activation energy, E, should increase linearly with the amount desorbed. The above figures, although indicating an increase, show clearly that the method is a very approximate one. However the magnitude of E is a reasonable one.

Alternatively the activation energy may be calculated by comparing the rates of evolution at equal coverage. If we represent the experiment thus



the activation energy can be found by comparing the slopes (1) and (2). Such slopes cannot be measured accurately as they are too slow and too rapid respectively, but they give an activation energy of about 30 kcal.mole^{-1}.

Using the procedure of experiment ≠ 117, experiments were performed on films saturated with combinations of nitrogen, hydrogen and ammonia. In each case the gases were allowed one hour to saturate the film. These experiments are summarised in table 4.6 and fig.4.15. The linearity of q against T is an important feature of these results. This linearity indicates that the Elovich theory is applicable.

When hydrogen was presorbed more hydrogen was evolved on warming to 278°K but the subsequent temperature steps did not produce "extra" hydrogen as can be seen by the near parallelism of the line for experiments 119 and 117 in fig.4.15. It should be stressed that, as the hydrogen adsorption took place at 348°K and thereafter the film was not raised above that temperature, the "extra" hydrogen evolved at 0°C resulted from interaction with or the presence of ammonia. Pre-adsorbed nitrogen drastically reduced the evolution of hydrogen and the experiment with simultaneous preadsorbed N_2 and H_2 gave somewhat more than hydrogen.

Experiment ≠ 119

This involved a film saturated with hydrogen at 348°K then ammonia at 195°K. Figure 4.16 shows the desorption of hydrogen with time and figs. 4.17 and 4.18 the p against log $(t + t_o)$ plots

Table 4.6

Expt	Dosing (a)molecule x 10^{-18} (b)order of addition (c)temperature of addition			Evolution of hydrogen (molecules x 10^{-17})		
	H_2	N_2	NH_3	T	n	$\sum n$
117			5.35	273	3.4	3.4
			(1)	291	2.77	6.17
			195°K	307	2.24	8.41
				327	2.36	10.77
119	4.56		4.14	273	6.08	6.08
	(1)		(2)	293	2.55	8.55
	348°K		195°K	307	2.35	10.98
				326	1.23	12.21
121		1.816	3.95	273	0.0	0.0
		(1)	(2)	291	.45	.45
		348°K	195°K	307	.83	1.28
				327	1.32	2.60
122	1.01	1.65	3.68	273	.76	.76
	(2)	(1)	(3)	290	1.05	1.81
	348°K	348°K	195°K	307	1.34	3.15
				327	1.75	4.90

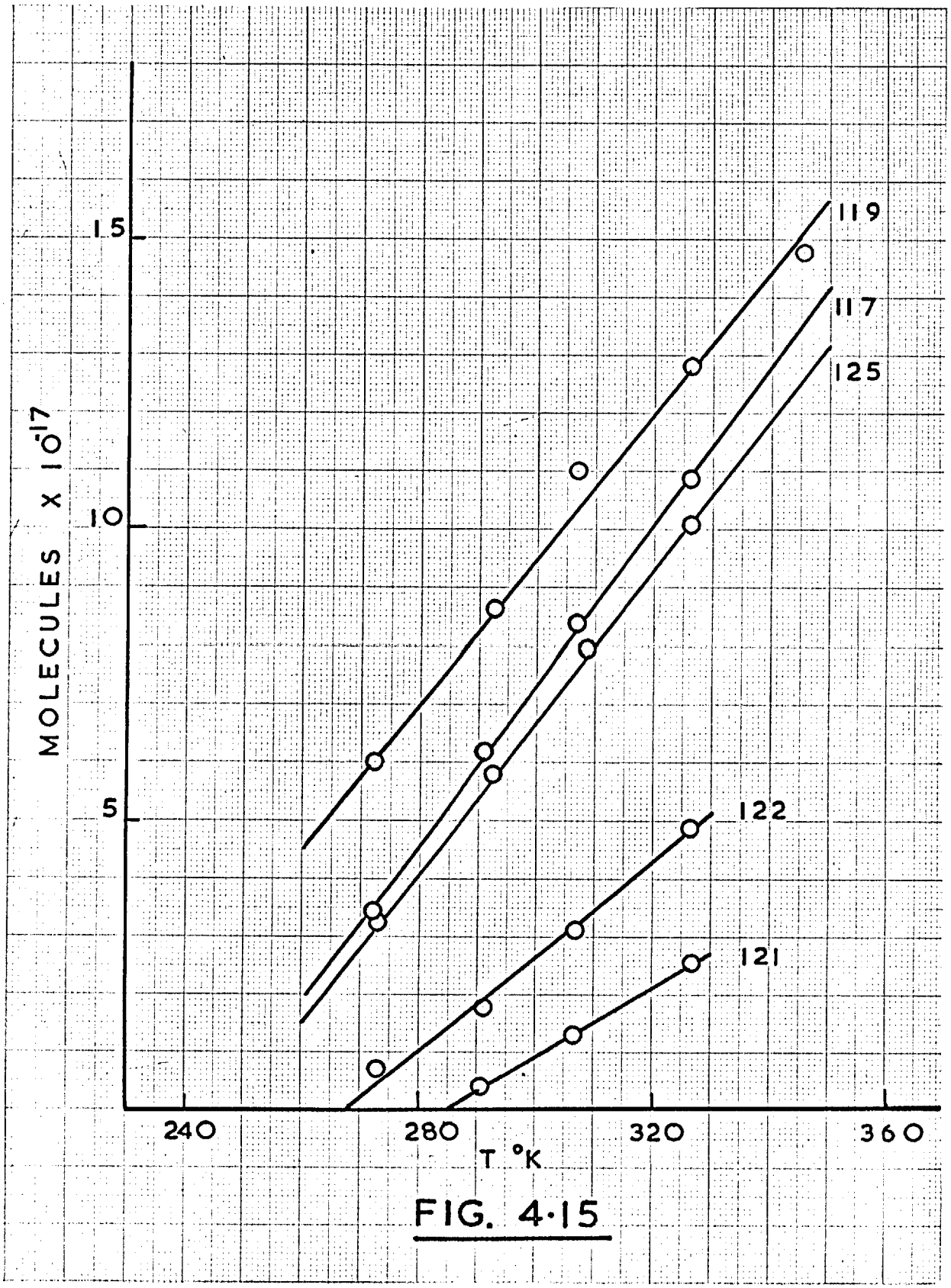


FIG. 4·15

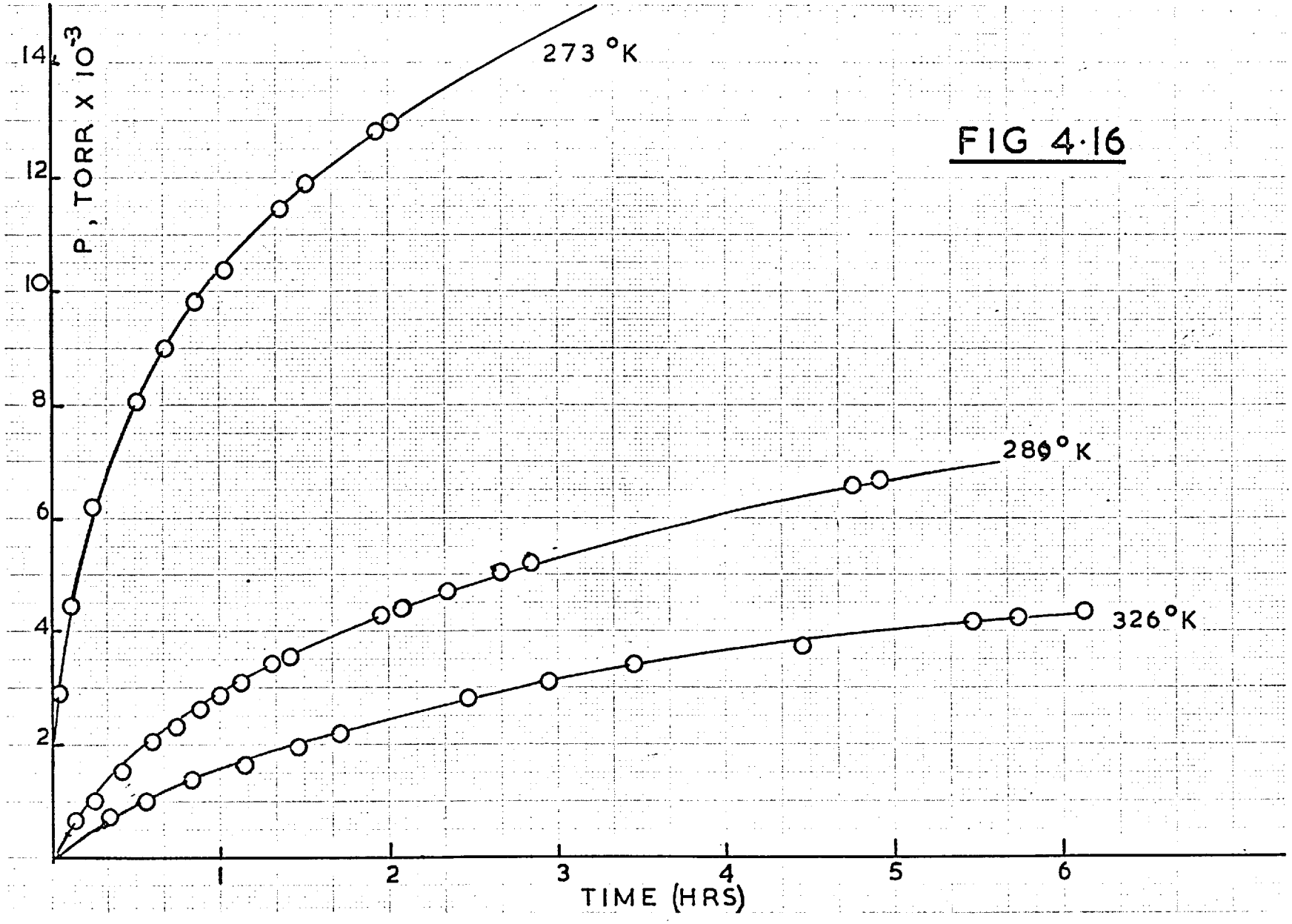


FIG 4·16

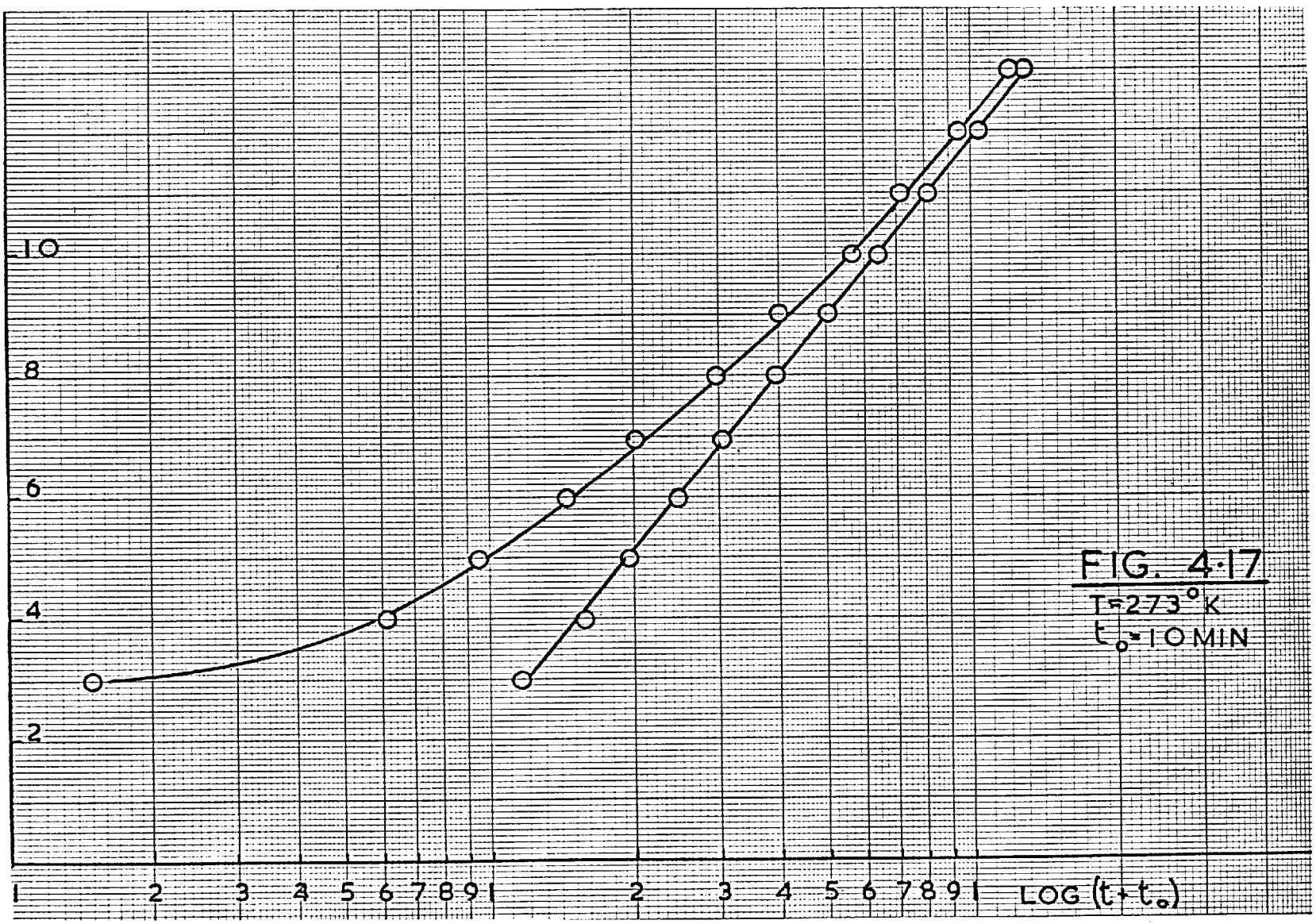


FIG. 4·17

T=273°K

t_0=10 MIN

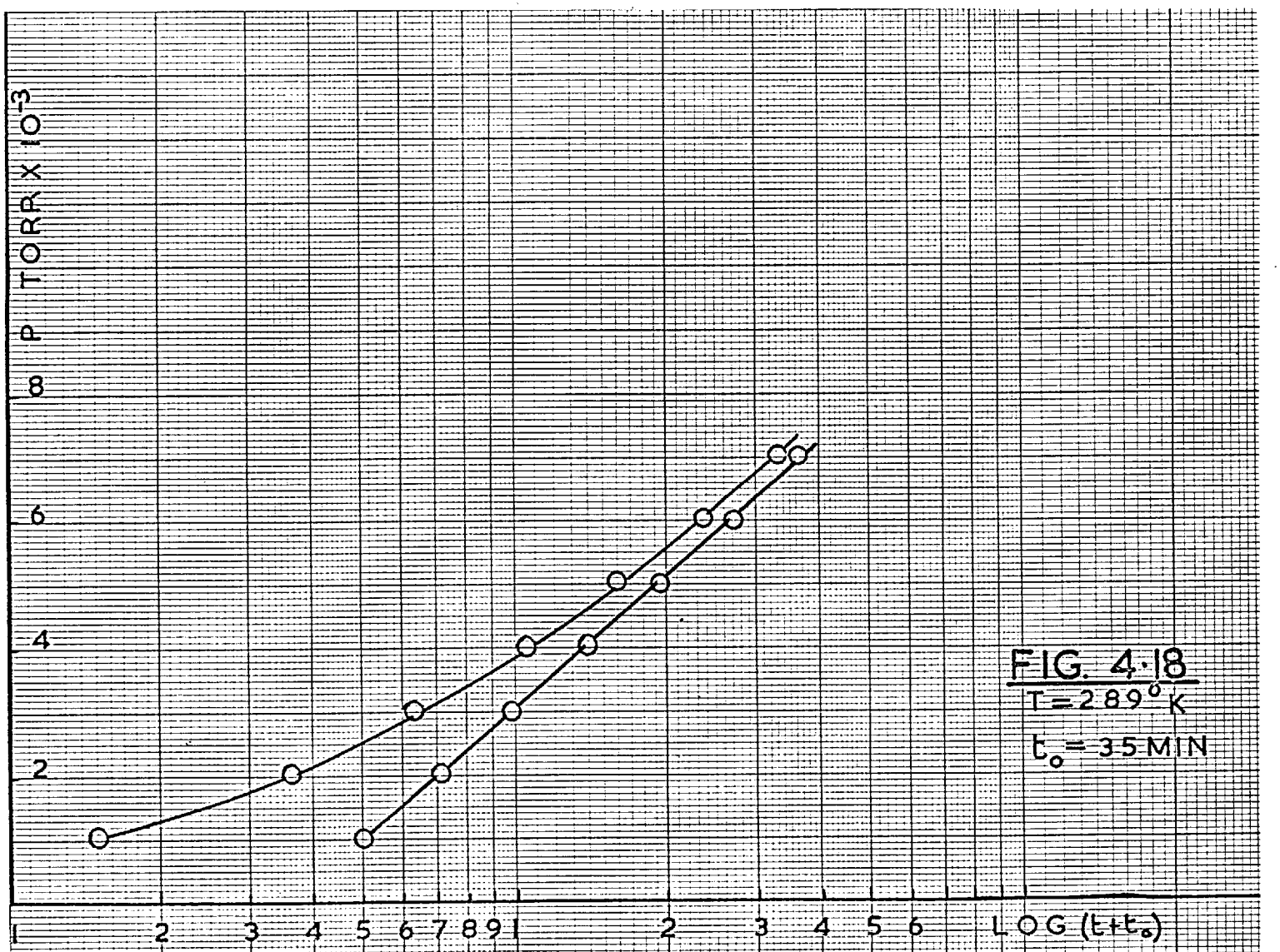
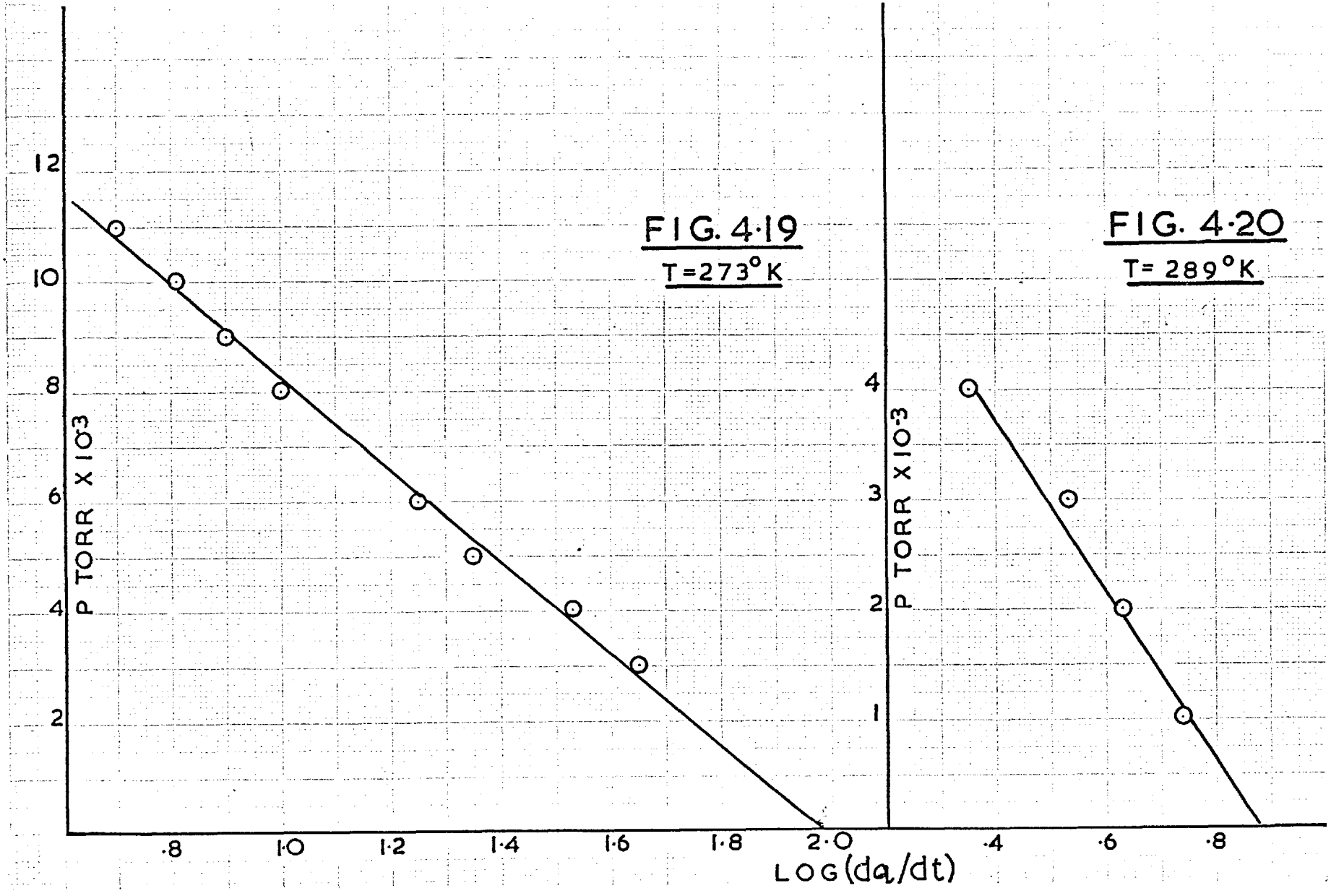


FIG. 4·18
T = 289° K
t_o = 35 MIN

which are again linear. From equation 4.8 ΔE at $q = 6.08 \times 10^{17}$ molecules was found to be 25.1 kcal.mole^{-1}. The average value of $(\partial E/\partial q)$ was calculated as 5.4×10^{15} cal.mole^{-1} molecules^{-1}. Plot of log (dq/dt) vs p (fig. 4.19 and 4.20) are again linear and give an average $(\partial E/\partial q)$ of 5.4×10^{15} cal.mole^{-1} molecules^{-1}. Thus the data from this experiment is very similar to that from ≠ 117 in which no hydrogen was pre-adsorbed.

Experiment 134

In this experiment hydrogen was desorbed from an ammonia layer (4.4×10^{18} molecules) in the same manner as used in experiment 117. Linear p as log $(t + t_o)$ plots were obtained and used in conjunction with equations 4.8 and 4.9 gave an average activation energy of 30.8 kcal.mole^{-1}. A total of 8×10^{17} molecules of hydrogen were evolved when the temperature reached 323°K. Following the removal of this hydrogen, the film was cooled to 195°K and a further 1.8×10^{17} molecules of ammonia were adsorbed. The temperature steps were repeated and the kinetic of desorption were as expected. Plots of log $(t + t_o)$ against p were linear as were dq/dt) against p plots. The average activation energy was 27 kcal.mole^{-1}. In view of the wide scatter in table 4.4 the difference of 3 kcal.mole^{-1} between this and the initial evolution activation energy is not significant. Again the hydrogen evolved at 323°K was pumped off and on re-cooling to 195°K ammonia (1.6×10^{18} molecules) was adsorbed. Tabulating the data :


12
10
8
6
4
2
P TORR X 10-3
.8
1.0
1.2
1.4
1.6
1.8
2.0
LOG(da/dt)
FIG. 4·19
T=273°K
4
3
2
1
P TORR X 10-3
.4
.6
.8
FIG. 4·20
T= 289°K

Step	NH_2 adsorbed at 195°K	total H_2 evolved at 323°K
1	4.4×10^{18}	$.8 \times 10^{18}$
2	1.8×10^{18}	$.6 \times 10^{18}$
3	1.6×10^{18}	

Experiments B2, B3 and B4

In the previous experiments one film was heated to various temperatures. It has been shown that the treatment of the results so obtained required certain assumptions. To avoid this three films were heated to 273, 281 and 289°K respectively and the evolution of hydrogen observed. In the case of the first two films following this evolution the films were raised to 289°K and the amount of hydrogen evolved after 12 hours measured. In this way the results of the three films were normalized. It was considered that this was superior to normalizing on the amount of ammonia adsorbed because this quantity is uncertain. Some ammonia considered "adsorbed" might be removed by pumping. From the normalized pressure vs time plots (fig. 4.21) rate of evolution dq/dt were found for each temperature at constant desorptions. These are shown in fig.4.22 from which activation energies can be calculated. A slight increase in ΔE with coverage is apparent; thus at $p = 3 \times 10^{-3}$ torr ΔE is 25.8 kcal.mole^{-1} and at $p = 8 \times 10^{-3}$ torr it is 27.6 kcal.mole^{-1}.

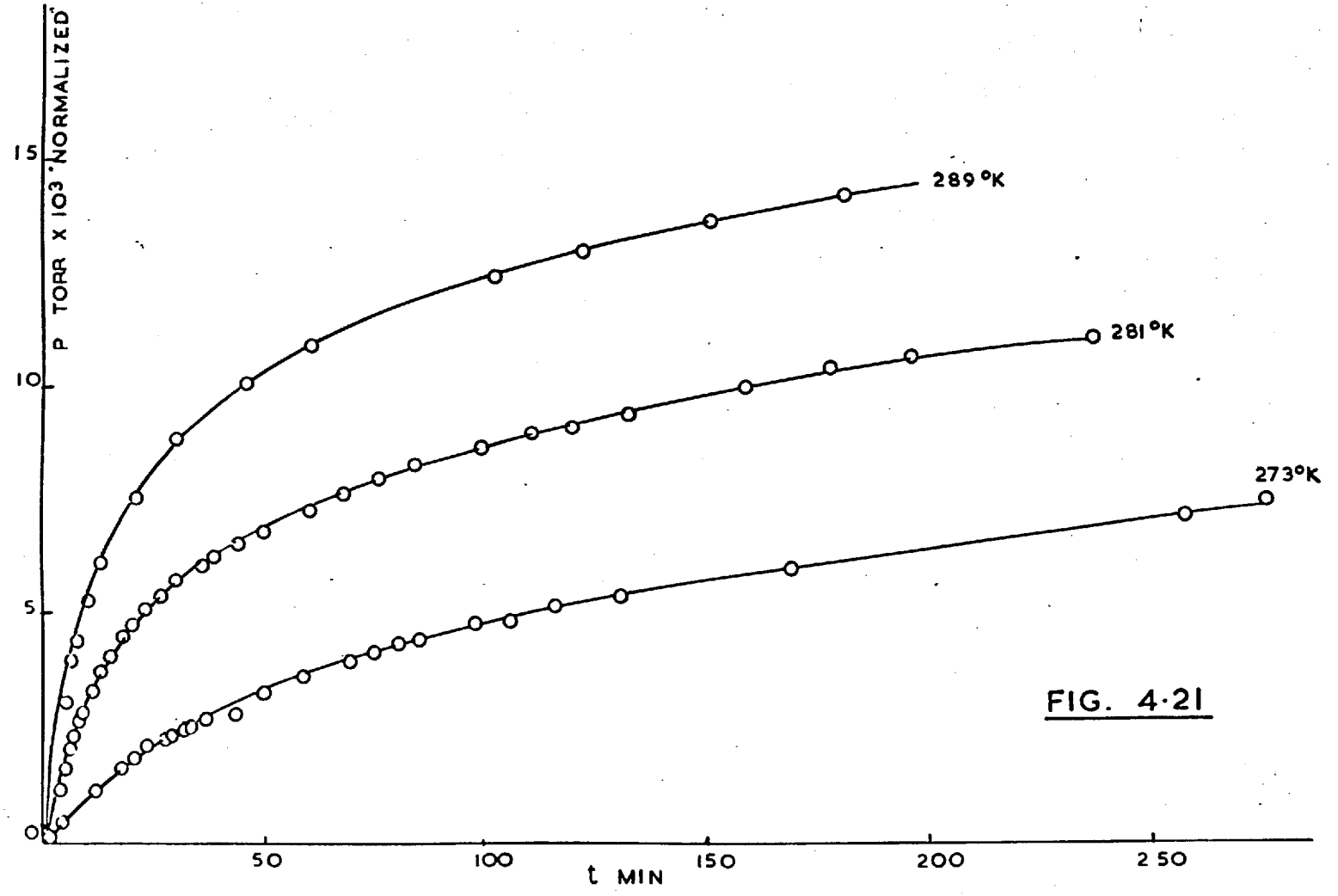

P TORR X 10³ "NORMALIZED"
15
10
5
0
289 °K
281 °K
273°K
50
100
150
200
250
t MIN

FIG. 4·21

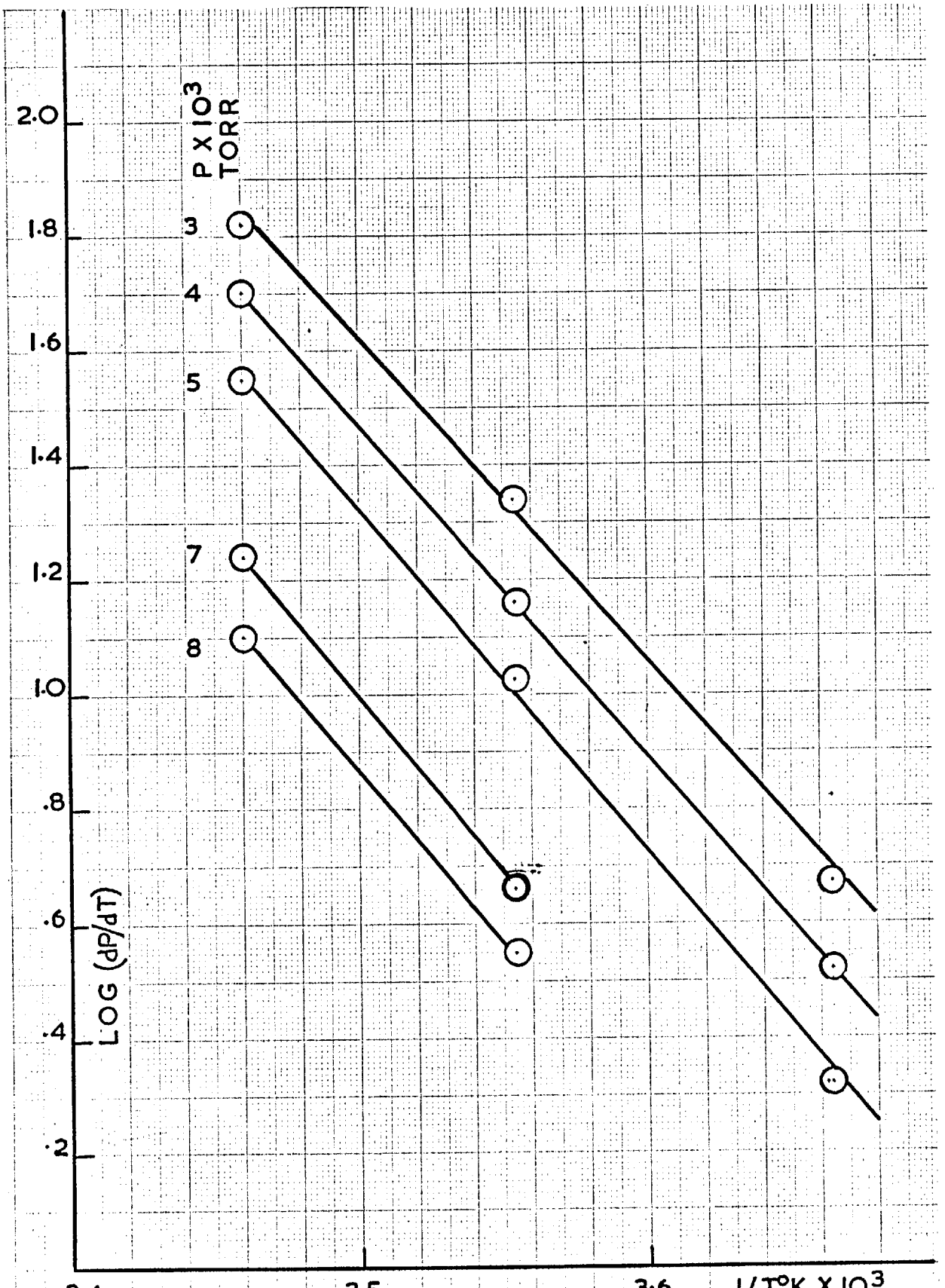

P X 10³ TORR
3
4
5
7
8
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
LOG (dP/dT)
3·4
3·5
3·6
1/T°K X 10³

FIG. 4·22

This corresponds to $\partial E/\partial q$ of about 1×10^{-14} cal.mole^{-1} molecules^{-1} which is in agreement with the value obtained from plots of log $(t + t_o)$ against p.

When plotted as a second order mechanism these experiments gave linear plots. However divergence from the straight line is apparent and is greater the higher the temperature. The slopes of these second order plots were the same for each temperature again showing the fruitlessness of the approach.

CHAPTER 5

THE DECOMPOSITION OF HYDRAZINE ON EVAPORATED TUNGSTEN FILMS*

These experiments were undertaken partly for their intrinsic interest and partly in an attempt to further elucidate the mechanism of ammonia decomposition.

5.1. Introduction

Hydrazine is interesting in that it has different possible modes of decomposition.

There have been but few studies of the decomposition of hydrazine catalysis and none of them involved metal films. The early experiments of Askey[191] indicated different reaction paths are taken by hydrazine decomposing on quartz and on heated wires of tungsten and platinum. On quartz the products indicated the reaction

$$3N_2H_4 \longrightarrow 4NH_3 + H_2$$

to have taken place; while the metals appear to have decomposed the hydrazine thus :

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

Krylov et al[187] have made a detailed study of the decomposition on mixed catalysts. Two reaction paths were suggested :

$$\text{(a)}\ 3N_2H_4 \longrightarrow 4NH_3 + N_2$$

$$\text{and (b)}\ N_2H_4 \longrightarrow N_2 + 2H_2$$

---

* This work was carried out in collaboration with J.M. Berak of the Institute of General Chemistry, Warsaw, Poland.

On semiconductors, acid catalysts and certain metal the evolution of ammonia and nitrogen was observed. The greatest activity was found with metals. It is interesting to note that an iron catalyst prepared for ammonia synthesis was the most active. Basic catalysts gave mainly hydrogen as the product. The authors suggested a chain radical mechanism. A recent study[192] of the decomposition of hydrazine on a single crystal of copper has shown the surface specificity of catalytic reactions. While the activation energy was 23.6 kcal/mole on both the (100) and (111) planes the rate of reaction on the (100) was twice as fast as on the (111). The products of decomposition were ammonia and nitrogen.

5.2. Experimental

5.2.1. Materials

Hydrazine 95% anhydrous hydrazine supplied by Eastman Organic Chemicals (U.S.A.) was dried and distilled from barium oxide in a stream of nitrogen. That fraction boiling between 110° and 112°C was collected and stored in the apparatus at 0°C. The purity of the hydrazine was checked by vapour pressure measurement using a manometer of carefully outgassed silicone oil. Good agreement with the literature data[193] was obtained.

Hydrogen and nitrogen Spectroscopically pure gases were used as supplied by B.O.C. in sealed bulbs.

Tungsten The same W wire was used as in ammonia experiments.

5.2.2. Procedure

The apparatus is shown diagrammatically in fig.5.1. The cell, traps and Pirani were baked out and the throwing filament outgassed in the manner described in §.2. The Pirani was operated immersed in ince. When the film had been thrown and annealed at 60°C traps T_2 and T_3, used to protect the film during throwing, were isolated as the low vapour pressure of hydrazine precluded their use. A measured quantity of hydrazine was admitted to and adsorbed by the film at 195°K. The film was then heated to a prescribed temperature.

To analyse the gas evolved ammonia was condensed in trap T_3 and simultaneous Pirani and McLeod readings taken for the permanent gas. The Pirani was calibrated for H_2, N_2 and mixtures thereof.

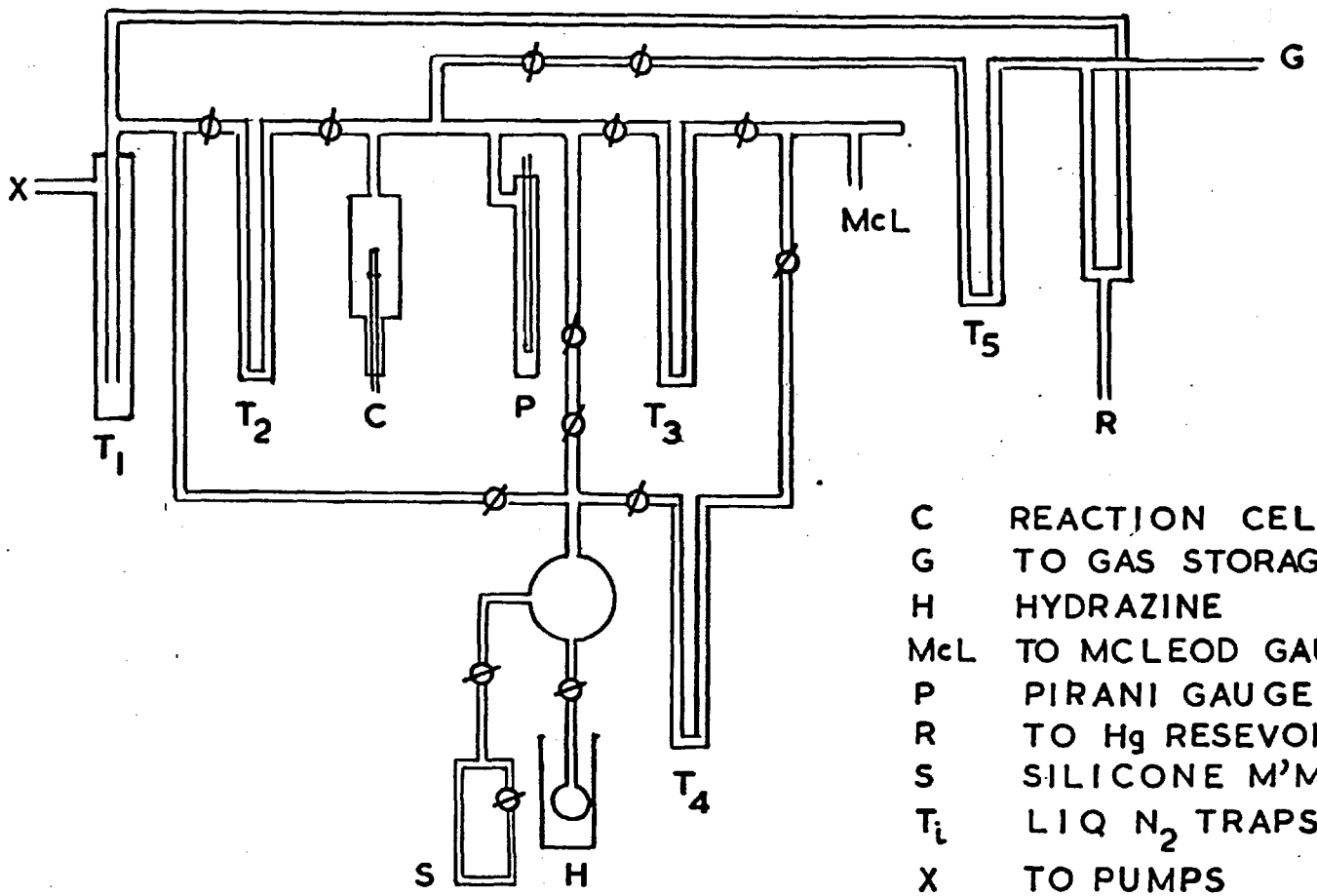
5.3. Results

5.3.1. Products

At all temperatures between 195°K and 273°K hydrazine reacted with the film to give a mixture of ammonia and hydrogen. Nitrogen was not detected in any experiment.

5.3.2. Kinetics of evolution

Figure 5.2 and 5.3 show the rates of evolution of ammonia and hydrogen respectively. A separate film was used for each temperature. To standardise the results the values are expressed as the percentage of hydrazine decomposed to ammonia and hydrogen respectively. The quantity of ammonia evolved exceeded that of hydrogen in all cases,



C REACTION CELL
G TO GAS STORAGE
H HYDRAZINE
McL TO MCLEOD GAUGE
P PIRANI GAUGE
R TO Hg RESEVOIR
S SILICONE M'METER
T_i LIQ N_2 TRAPS
X TO PUMPS

FIG. 5.1

but the ratio $\left[NH_3/H_2\right]$ decreased with time.

Figure 5.4 shows the evolution obtained from one film raised to increasing temperature, and fig.5.5 shows the amounts of ammonia and hydrogen desorbed from a film which had presorbed hydrogen at 273°C. Detailed values of the amount of ammonia and hydrogen desorbed from both films are given in table 5.1. The quantity of hydrazine chemisorbed on the clean film was 34.5×10^{-7} moles and on a film which had adsorbed 36.4×10^{-7} moles of hydrogen 16.2×10^{-7} moles of hydrazine were adsorbed.

5.3.3. Activation energies

Figure 5.6 shows the amount, expressed as a percentage of the hydrazine desorbed, of ammonia and hydrogen desorbed from the films at different temperatures.

The observation that the amounts of both hydrogen and ammonia increased linearly with temperature suggested an increasing activation energy. Thus the Elovich[190] equation can be applied

$$\frac{dq}{dt} = a \exp\left(-\frac{bq}{RT}\right)$$

where q is the quantity of desorbed gas and b the constant relating this to the activation energy for desorption. From this equation we can derive

$$\log\left(\frac{r_1}{r_2}\right)_{q=const.} = \frac{\Delta E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

when $r_i = (dq/dt)_{T_i}$. The activation energies for hydrogen desorption from this are 13.4 kcal/mole and 9.6 kcal/mole for "clean" and "hydrogen covered" films respectively.

Table 5.1

Desorption of H_2 and NH_3 from "clean" and "hydrogen-covered" film (moles x 10^{-7}).

Temp. °C	Time mins	"clean film"		"hydrogen-covered film	
		H_2	NH_3	H_2	NH_2
-78	10	0.003	0.133	0.108	0.051
	30	0.038	0.219	0.325	0.051
	55	0.080	0.310	0.566	0.052
-50	10	0.273	2.618	2.886	0.917
	30	0.424	3.422	4.635	0.922
	55	0.587	3.938	5.065	0.930
-42	10	0.310	0.605	1.428	0.195
	30	0.636	0.903	3.418	0.408
	55	0.965	1.194	5.638	0.670
-23	10	0.797	1.397	4.589	0.654
	30	1.611	2.076	7.676	1.109
	55	2.317	2.445	9.826	1.574
0	10	1.257	0.697	1.507	0.504
	30	1.775	0.826	1.939	1.002
	55	2.116	0.895	2.396	1.482
Total amount at 0°C		6,063	8.772	23.493	4.709

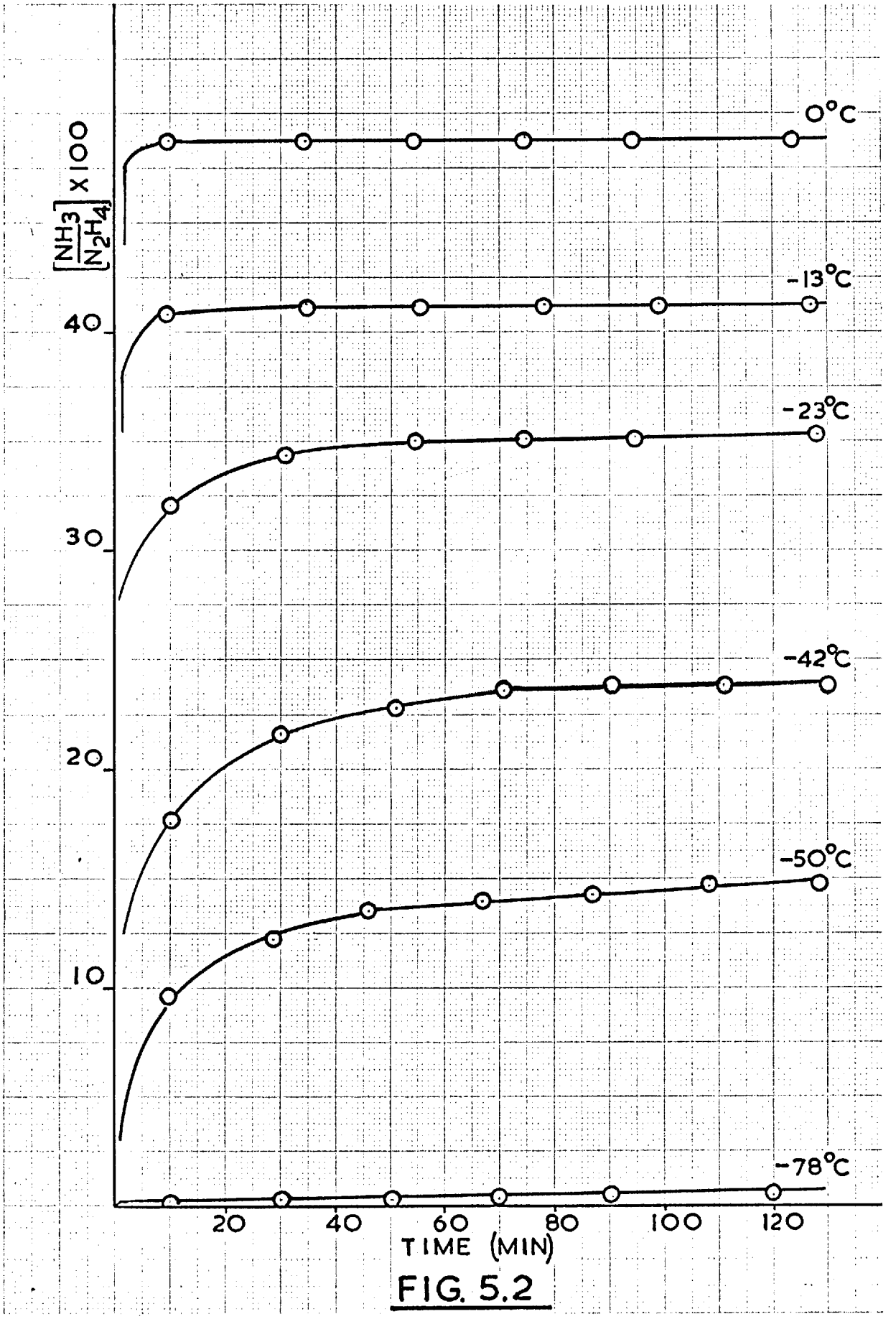

$\frac{[NH_3]}{[N_2H_4]} \times 100$
40
30
20
10
0°C
-13°C
-23°C
-42°C
-50°C
-78°C
20
40
60
80
100
120
TIME (MIN)

FIG. 5.2

FIG. 5.3

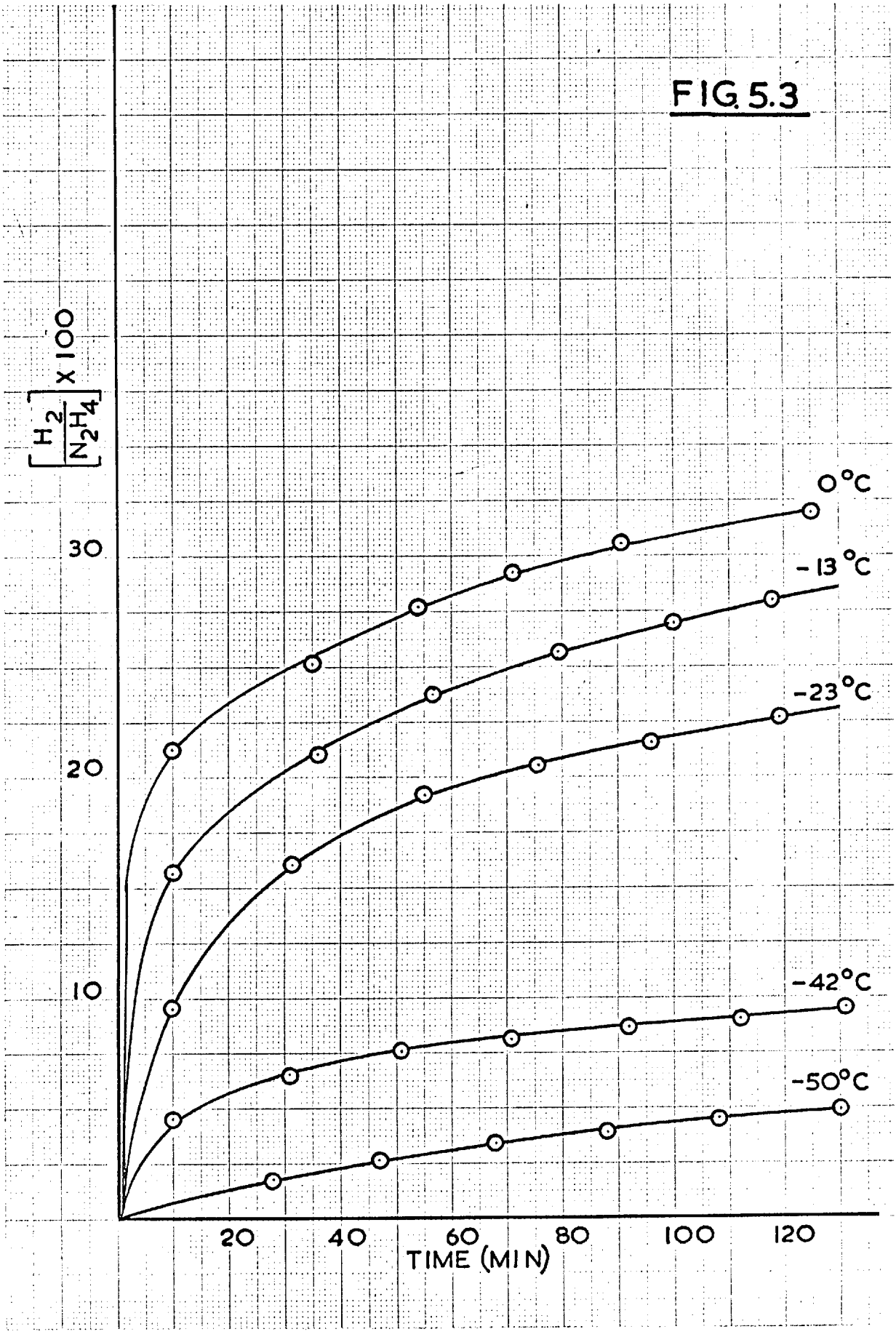

$\left[\frac{H_2}{N_2H_4}\right] \times 100$
30
20
10
0°C
-13°C
-23°C
-42°C
-50°C
20
40
60
80
100
120
TIME (MIN)

FIG. 5.4

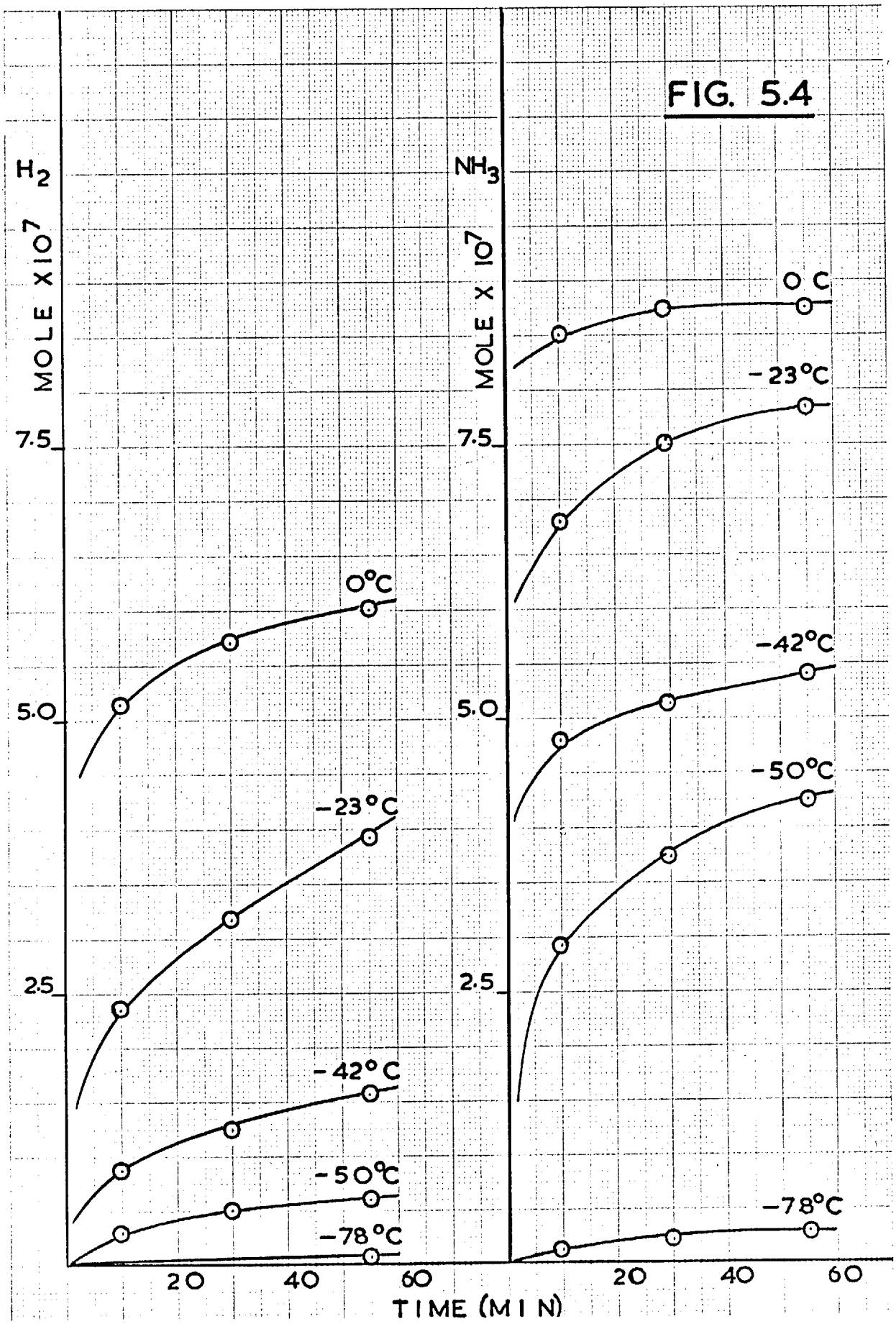

H2
MOLE X 10^7
7.5
5.0
2.5
0°C
-23°C
-42°C
-50°C
-78°C
20
40
60
NH3
MOLE X 10^7
7.5
5.0
2.5
0 C
-23°C
-42°C
-50°C
-78°C
20
40
60
TIME (MIN)

FIG. 5·5

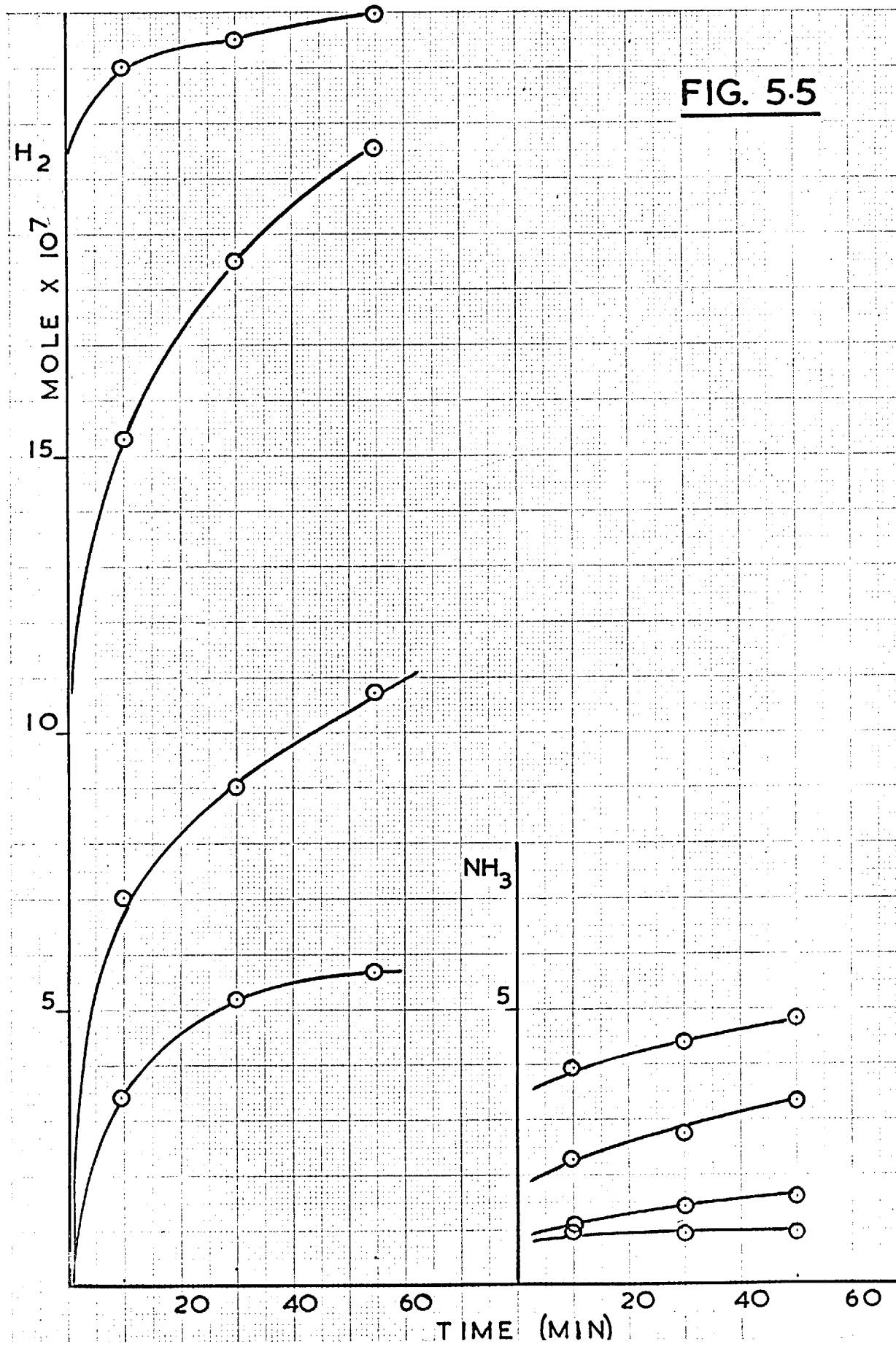
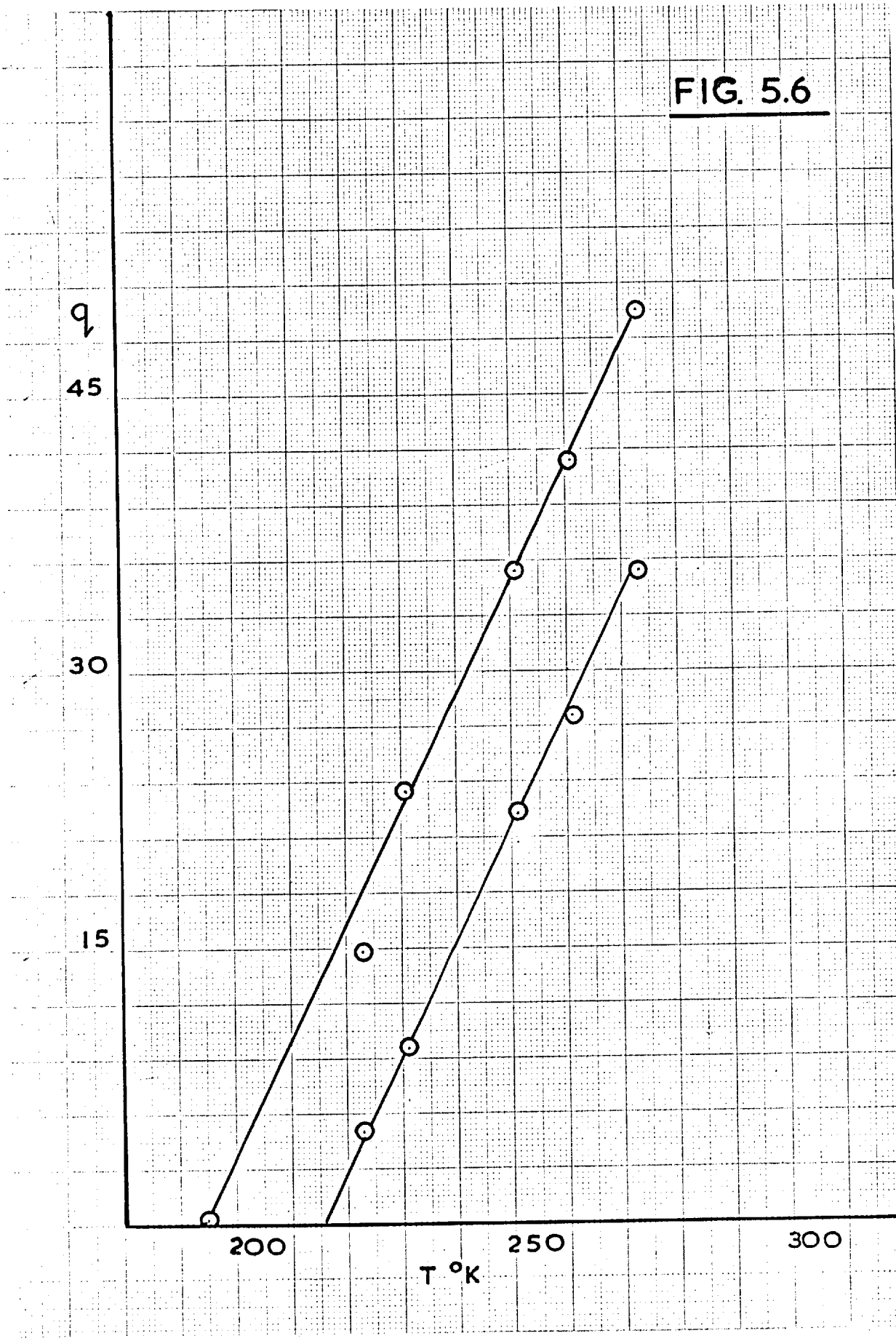
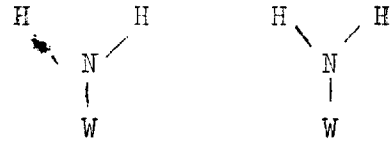


FIG. 5.6

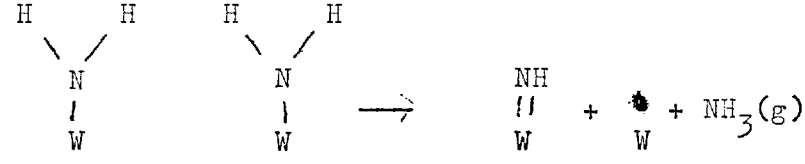


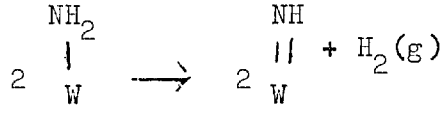
5.4. Discussion

The dissociation energy $D(H_2N\text{-}NH_2)$ was originally thought to lie between 19 and 24 kcal/mole[193]. A recent evaluation[194] has increased this to 60 kcal/mole which is still low compared with the 103 kcal/mole for D(H-H). If the metal-amine bond energy is comparable to that of metal-hydrogen atom then the hydrazine will be dissociatively adsorbed as



There are two possible modes in which these radicals can decompose on warming :

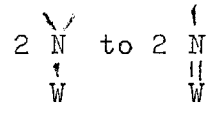
1. 

and 2. 

The first of these is energetically more favourable. The breaking of the H-NH bond is compensated by the formation of $H\text{-}NH_2$. Hence the energy change (activation energy) for reaction (1) will be the heat of adsorption of ammonia less the bond energy difference between $W\text{-}NH_2$ and W=NH. At zero coverage the heat of adsorption of ammonia on tungsten is about 70 kcal/mole[17] if adsorption is not dissociative.

The difference in the bond energy W-N and W=N is assumed to be equal to the difference between D(N-N) and D(N=N) i.e. 62 kcal/mole. The activation energy will be about 8 kcal/mole at zero coverage. At higher coverages, the reaction to give ammonia gas is still more favourable as the adsorption energy falls as θ increases. The desorption of ammonia was indeed too rapid for us to calculate activation energies.

The formation of hydrogen, however, requires the breaking of 2 N-H bonds and the formation of one H-H bond, a total energy requirement of 100 kcal/mole. This is offset by the transformation of



i.e. a possible gain of 124 kcal/mole. But the activation energy is 13 kcal/mole thus the transformation can contribute only 87 kcal/mole. The change from N-W to N=W involves a change of 44 kcal/mole. Hence the ammonia evolution will occur only if its heat of adsorption is 40 kcal/mole.

The results for the film having presorbed hydrogen are of interest. In general, the areas of separate films differed by not more than 20%. On two separate films 34.5×10^{-7} moles of N_2H_4 and 36.4×10^{-7} moles of H_2 respectively were adsorbed. Thus assuming the same areas, 1 molecule of N_2H_4 occupies 2 sites as required by one hydrogen molecule. This indicates that the

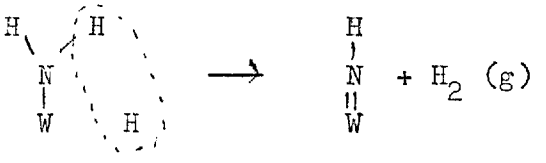
assumption of dissociative adsorption is a reasonable one. On the "hydrogen covered" film only 16.2×10^{-7} moles of hydrazine were adsorbed. This perhaps reflects the lower heat of adsorption as the surface coverage is increased. For this N_2H_4 to be adsorbed at least part of the hydrogen must be held interstitially.

If the amounts of ammonia desorbed from the "clean" and "hydrogen covered" films are calculated and expressed as the faction of N_2H_4 on the surface we obtain :

"clean"	0.25
"hydrogen covered"	0.29

Hence apparently the same proportion of ammonia is desorbed and therefore the same mechanism is operative in each case.

However the mechanism of hydrogen evolution is different and probably takes place as



The amount of adsorbed hydrazine not reacted to give ammonia amounts to $(16.2 - 4.7) = 11.5 \times 10^{-7}$ moles and if all reacted to give hydrogen this would yield $2 \times 11.5 \times 10^{-7}$ or 23×10^{-7} moles. In fact, 23.5×10^{-7} moles were obtained in this experiment, a very good agreement.

Some hydrogen still remains on the surface, this amount being $36.4 - \frac{1}{2}(23.5) \sim 24.3 \times 10^{-7}$ moles. This corresponds to a 70% coverage; this would be a reasonable figure for hydrogen desorption

from a tungsten film covered only with hydrogen. The radical left on the surface is -NH and it occupies about 67% of the surface. Clearly this radical does not react easily with the hydrogen atoms remaining on the surface. While the calculations above indicated a lower activation energy for desorption from a "hydrogen covered" film compared to the "clean film", a direct comparison is not very meaningful since ΔE is a function of coverage. It is difficult to calculate the coverage of H_2 to which the calculated ΔE values apply. But it is clear that hydrogen is evolved more easily from the "presorbed hydrogen" surface. This is expected since the bond energy H-W (ca 75 kcal/mole) is less than the energy to break the second N-H bond (ca 100 kcal/mole).

CHAPTER 6

DISCUSSION

Felix qui potuit rerum cognocere causam

Virgil

6.1. The Surface Potential Results

At the outset of this work it had been hoped that by adding hydrogen and nitrogen to an ammonia layer on tungsten the resulting shift in the equilibrium

$$NH_3 \rightleftharpoons NH_2 + H$$

could be studied by surface potential measurements. It cannot be claimed that any of the experimental results can be so simply interpreted.

It has been established that the maximum surface potential of ammonia on tungsten is 1.9 ± 0.1 V at $195^{\circ}K$. This may be compared to a saturation value of + 2.1 V for ammonia on an evaporated nickel film[141]. The maximum surface potential was developed when the tungsten had taken up 4×10^{17} molecules of NH_3. Further addition of ammonia up to chemisorption saturation at ca 5×10^{18} molecules produced no further change. This behaviour is normal because the anode current is controlled entirely by the outer surface. This outer surface will approximate to the geometric area. Further molecules enter the inner surface and do not affect the surface potential. The Helmholtz equation

$$\Delta\phi = 4\pi \sigma \Theta \mu$$

predicts that ammonia, having a permanent dipole of 1.45 D, would have a surface potential of +2.8 V if one assumes the molecules are hexagonally close packed with the positive pole outward and the cross section area of the molecule is that generated by rotating the molecule about the N atom as pivot. Using bond distances of H-H = 1.645 Å and N-H = 1.016 Å with the N atom 0.36 Å above the HHH plane the diameter works out as 1.90 Å. The Helmholtz equation also assumes the molecules are perpendicular to the surface. It has been pointed out[141] that, statistically, the molecules might be aligned head to tail alternately. Such a model is viable when one considers the ease with which the N atom flips through the HHH plane[181]. This would give a zero dipole. But the large polarizability of ammonia would give a large induced dipole, independent of the direction of the permanent dipole. From a consideration of the electronic structure of ammonia, it seems feasible that it could be bonded to the surface by the lone pair of the nitrogen. If this were the case the "flipping" would be removed. Chemisorption by charge transfer was previously[141] ruled out for Ni/NH_3 because of the time dependence of the surface potential measured an admission of an ammonia dose.

It was argued that such a process would not be an activated one. Although time dependence was again observed this can now be attributed to the slow diffusion of ammonia through the cold traps before it enters the cells. Saturating the glass with

ammonia prior to throwing the film significantly reduced this dependence. The differential heat curves for ammonia is about 20 kcal.mole^{-1} higher at all coverages than that for hydrogen at room temperature[19], and ranges from 70 to 40 kcal.mole^{-1}. The high heat at low coverage is no doubt associated with the lone pair bonding and the large face of ΔH with θ reflects, in part, the large dipole repulsion of similarly oriented NH_3 (a) and provides the reason why NH_3 cannot be adsorbed on adjacent sites (see also §6.2). Magnetic and resistance measurements might give some interesting results as the addition of the lone pair to the metal conductance band should have an effect on these properties.

Considering the somewhat idealised conditions implied by the Helmholtz equation the value of 1.9 V compares favourably with the calculated value of 2.8 V. Co-operative effects would account, at least partially, for the divergence. It should also be pointed out that physical adsorption, which is generally the case giving a positive surface potential, is eliminated by the observation that prolonged pumping at 195°K did not change the surface potential.

The variation of surface potential with increasing temperature can be explained in terms of dissociation. It has been clearly established that above 273°K the ammonia decomposed to give hydrogen. In fig.3.9 is shown the variation of the surface potentials of films showing the maximum surface potential at 195°K.

The decrease can be explained by assuming that the transition of an NH_3 molecule to an amino radical-NH_2 is accompanied by a decrease in dipole. It seems probable that the -NH_2 dipole is positive but less so than that of the NH_3 molecule. Thus as dissociation proceeds the surface potential will become less positive. Because the outer surface is full the hydrogen so formed will enter the inner surface and have no effect on the surface potential. We can no longer ascribe to the, albeit tentative, assumption[141] that an NH_2 radical has a surface potential equal and opposite to that of a hydrogen atom. This was suggested by the fact that initial doses of ammonia gave no surface potential change. It has been shown above that this is not so when the apparatus was previously saturated with ammonia.

When the ammonia loading was less than that required to give a maximum surface potential ($\neq$ 95 in fig.3.9) an increase in the temperature gave a slightly steeper decrease. As the outer surface was not completed the hydrogen was able to occupy sites on the surface and the negative surface potential of these atoms caused the surface potential to be decreased correspondingly.

The partial recovery of the surface potential when the film was allowed to stand for a long time at the lower temperature perhaps reflects the low mobility of the hydrogen atom giving a slow reaction $NH_2 + H \longrightarrow NH_3$. When more ammonia was added the recovery was completed because the adsorbed ammonia was able

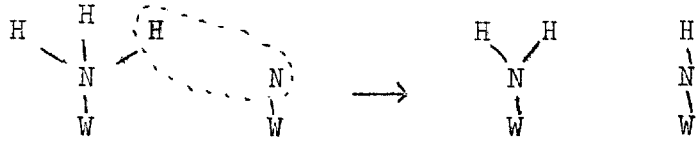
to re-establish the surface equilibrium for that temperature by surface reactions.

The results of the pre- and post-addition experiments can also be explained in terms of inner and outer surfaces. When ammonia was adsorbed on top of hydrogen or nitrogen it seems justifiable to assume that ammonia would be preferentially adsorbed on the outer surface by virtue of its greater size. Conversely H_2 or N_2 adsorbed on top of ammonia would be accommodated in the inner surface. In both cases the result is the same viz. an outer layer of ammonia molecules. The surface potentials were therefore the same as for a film having only ammonia adsorbed on it.

The inter-addition results are interesting. The initial decrease with hydrogen (fig.3.13) is most simply considered as the contribution of the negative surface potential of hydrogen to the average surface potential. At this stage there was room on the outer surface to accommodate the hydrogen. The subsequent increase in surface potential was due to protonic hydrogen, i.e. hydrogen held between the chemisorbed groups at a distance of ca 1 Å from the metal surface with a virtual positive charge of about half the protonic charge. The large positive change obtained when hydrogen was added to a film having a saturated layer of chemisorbed oxygen[146] was attributed to protonic hydrogen. That the stage at which hydrogen was added (post, pre or inter) determined the surface potential is in keeping with the

observation[160][198] that the order of addition determined the surface potential for the CO + H + Ni system.

The positive effect obtained with pre-addition of nitrogen, obviously, cannot be so explained. Had we subscribed to the idea that ammonia is dissociatively adsorbed this positive effect could be attributed to nitrogen/hydrogen atom interaction. However, other results rule out dissociative adsorption at 195°K. It is interesting to consider the possibility of ammonia/nitrogen interaction



where the amino species has a small positive dipole. That it is small is suggested by the comparatively large amount of nitrogen added to give a small surface potential change. This is consistent with the view expressed above that the dipole of NH_2 is positive but less so than that of NH_3.

This reaction would not prevent subsequent addition of ammonia from building up an NH_3 layer on the outer surface with N or NH species in the inner surface, thus finally giving a surface potential identical to that obtained with NH_3 on a clean surface. The behaviour of nitrogen is problematical. We have seen in section 1.6.5 that the surface potential of nitrogen on clean tungsten is a point of discussion. Delchar[199] has recently

shown that the sign of the surface potential obtained is a function of the crystal plane upon which adsorption occurs. It may well be that the ammonia in the inter addition experiments forces the nitrogen to take up sites upon which it has a positive surface potential rather than the negative one we observed on a clean surface. Again perhaps the nitrogen is adsorbed on top of the ammonia as molecules just as nitrogen in the γ state is adsorbed on top of β species.

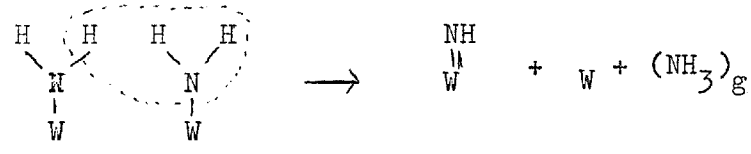
The interaction of $NH_3/H_2/N_2$ on the film has been complicated by the fact that only the outer surface was covered. The inner surface was free to adsorb various species and hence remove them from observation. It might have been more interesting had it been possible to work with saturated or near saturated films. However, as discussed in Chapter 3 this was not possible as the emission filament itself caused surface reactions at high coverage. There was no evidence for such reactions at low coverage; surface potentials remained constant over long periods with the emission filament on. While an emission filament coated with lanthanum hexaboride did have a lower working temperature it still caused hydrogen to be evolved at high ammonia coverage when adsorbed hydrogen was present.

6.2. Kinetic Experiments

We have shown in Chapter 4 that the evolution of hydrogen from ammonia adsorbed on a tungsten film cannot be treated in terms of a simple second order reaction. An analysis in terms

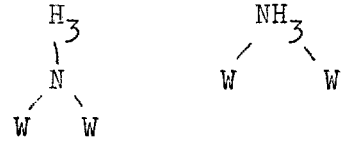
of a heterogeneous surface has given an activation energy of about 25 kcal.mole^{-1}. The value of (oE/oq) was found to be about 7 x 10^{-15} cal.mole^{-1} molecules^{-1}. This treatment has been successfully applied to hydrogen atoms recombination followed by molecular hydrogen desorption from a nickel film[200]. Here ($\partial E/\partial q$) was found to be 8 x 10^{16} cal.mole^{-1} molecules^{-1} with an initial activation energy of 0.79 kcal.mole^{-1}.

The rapidity of ammonia evolution from a tungsten film which had adsorbed hydrazine indicates that the two NH_2 radicals on adjacent sides react very readily to give ammonia

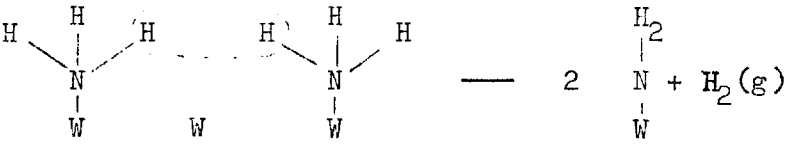


This suggests that ammonia does not give two such adjacent radicals on adsorption. Therefore the ammonia molecules are adsorbed on every other site and thus do not give adjacent NH_2 radicals on decomposition.

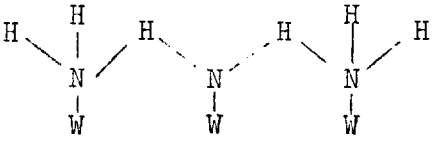
or possibly with the nitrogen in a pentavalent state



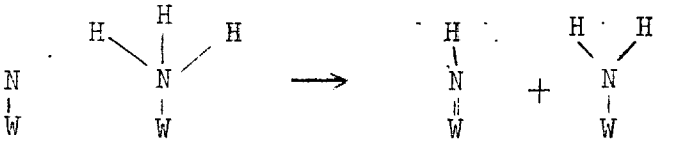
Evolution of hydrogen would then take place as



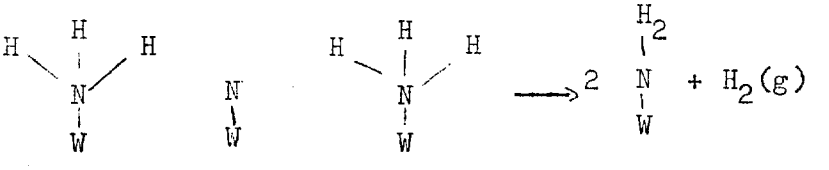
The "excess" hydrogen evolved at 273°K from a tungsten film saturated with H_2 and NH_3 (≠ 119) could have resulted only from the interaction of the ammonia for the "presorbed" hydrogen was added at 348°K. It is postulated that the ammonia weakens the adsorption of the interstitial hydrogen on the low adsorption potential sites and consequently some is adsorbed on raising it to 273°K. The amount of hydrogen evolved thereafter follows that for ammonia-only-experiments (viz the parallel plots for ≠ 119 and ≠ 117 & 125). With presorbed nitrogen the H atoms of the ammonia weakly attracted by the nitrogen atoms



On warming to 273°K there is a competition between



and



The reversible adsorption of hydrogen on a partially decomposed ammonia layer is not merely the occupancy of vacant sites created by the decomposition. This can be seen from the figures of table 4.1. While there appears to be a trend for more hydrogen to be readsorbed it does not increase with the amount of decomposition. Thus at 195°K following "step 273" the hydrogen readsorbed amounted to ca 50% of that evolved while after "step 307" this was to ca 25%. As decomposition proceeds the activation energy increases and hence by analogy the activation energy for hydrogen adsorption may be considered to increase. If this is so only sites of low activation energy will adsorb hydrogen. The rate of adsorption is given by

$$r_a = p(1 - \theta) \exp - (E/RT)$$

and the rate of desorption by

$$r_d = \theta \exp - (\Delta H + E)/RT$$

when E is the activation energy at ΔH the heat of adsorption. Thus at equilibrium

$$p(1 - \theta) \exp - (E/RT) = \theta \exp - (\Delta H + E)/RT$$

from which it will be seen that E cancels out and adsorption isotherms are sensitive only to ΔH. We cannot therefore estimate the activation energy.

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